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SUMMARY

Work during this period has continued in all areas previously reported.

Apparatus for measurement of chemiluminescent and fluorescent quantum yields, ~~described in the last report~~, has been fully calibrated. Measured values for fluorescence yield of standard systems at low concentrations agrees with literature reports, thus confirming the over-all calibration. New data on fluorescence at higher concentrations have been obtained for later use. A quantum yield of 6% was measured for an improved oxalyl chloride system, and 1% for several 3-aminophthalhydrazide systems.

Three earlier synthetic approaches were deferred to the third quarter, two were abandoned and a route to a chemiluminescent polymer appears to have been found. Three new synthetic approaches are being attempted and are in progress. Two of these involve routes to compounds which should eject nitrogen in an energy producing step. These will test possibilities for chemiluminescence when oxygen is neither a product nor a reactant. A new route designed to lead to a highly fluorescent 3-aminophthalhydrazide derivative is also reported.

Kinetic, electrochemical and electron spin resonance studies of the 3-aminophthalhydrazide reaction suggest that the first step involves a one electron oxidation to produce a radical intermediate

which then can react with oxygen or a peroxy radical to give peroxidic chemiluminescent precursors or ~~can~~ lose another electron to produce a non-luminescent material.

Evidence for the formation of  $\text{HOOC}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\overset{\overset{\text{O}}{\parallel}}{\text{O}}\text{H}$  as an intermediate in the oxalyl chloride-hydrogen peroxide chemiluminescence is given. This led to the discovery of a new chemiluminescent reaction based on forming the same intermediate. Chemiluminescence then occurs by a free radical induced chain decomposition of the intermediate in the presence of a fluorescing agent. A partial mechanism for this reaction is proposed and discussed.



### INTRODUCTION

Technical Report No. 1 states the objectives and approaches of this program and covers the first three months' work. The reader is referred to that report for the rationale used to select systems whose investigation began during the period of the first report.

This report reviews the work of the second three months and presents the work in three sections: I. Reaction Mechanisms (studies which attempt to elucidate the nature of selected chemical reactions in which an electronic excited state is formed), II. Structural Criteria for the Formation of Electronically Excited Molecules (proof of mechanism by synthesizing and studying the behavior of specially designed molecules) and III. Spectroscopy and Energy Transfer (quantitative measurements of light emission and methods for transferring excited state energy from one molecule to another).

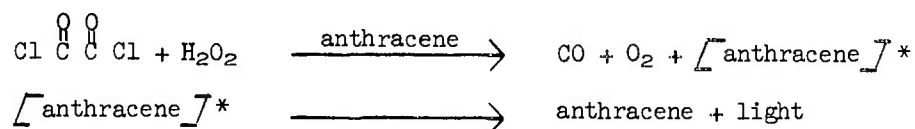
SECTION I

REACTION MECHANISMS IN CHEMILUMINESCENCE

A. The Reaction of Oxalyl Chloride with Hydrogen Peroxide in the Presence of a Fluorescent Acceptor.

Introduction

Oxalyl chloride reacts vigorously with hydrogen peroxide to produce carbon monoxide, oxygen, and hydrochloric acid with little emission of light<sup>1</sup>. When carried out in the presence of a fluorescent compound, however, the reaction generates a bright light at least approximately matching the normal fluorescence emission of the fluorescent compound<sup>1</sup>.



This reaction is of substantial interest because of the implied energy transfer process whereby chemical energy produced by the oxalyl chloride-hydrogen peroxide reaction appears as singlet electronic excitation energy in the fluorescent compound. The reaction is also unusual in that organic chemiluminescence is customarily derived from more complex systems. The preceding report in this series presented some preliminary experimental results bearing on the energy transfer process<sup>2</sup>. Summarized below are recent results bearing on the over-all mechanism.

## Results

### (a) Reaction Conditions

The reaction as reported in the literature<sup>1</sup> (one molar oxalyl chloride in dioxane added to 30% aqueous hydrogen peroxide in dioxane containing the fluorescent acceptor) provides a bright flash consistent only with a very low quantum yield. However, we find that the same reaction at -60° to -70° provides much stronger emission with lifetimes up to 5 minutes. Moreover, addition of oxalyl chloride to dilute anhydrous ethereal hydrogen peroxide gives a very strong emission lasting up to several minutes even at room temperature. Under these latter conditions the quantum yield for an initial very small charge of oxalyl chloride can be on the order of 3% and even this value may be subject to improvement (see Section III).

### (b) Free Radical Chain Inhibition

In experiments where free radical inhibitors were added in low concentration to chemiluminescent reactions already in progress, the emission was quenched by hydroquinone, 2,6-ditert-butyl-4-methylphenol, dibutylsulfide, and by dilauryl thiodipropionate. Thus chemiluminescence evidently results from a free radical chain reaction<sup>3</sup>.

### (c) Oxalyl Chloride Concentration

The efficiency decreases substantially at high oxalyl chloride concentrations. (The effect of reactant and acceptor concentrations on quantum yield will be determined quantitatively in the near future.)

(d) Reaction Stoichiometry

A standardized 0.1 molar solution of anhydrous ethereal hydrogen peroxide containing 9,10-diphenylanthracene was titrated with a standardized 0.1 molar solution of oxalyl chloride until additional oxalyl chloride failed to generate chemiluminescence. After each incremental addition of titrant the mixture was allowed to stand until the luminescence decayed before continuing the titration. The inverse titration was also carried out by the same procedure. Both procedures indicated that the stoichiometry is nearly 1:1.

(e) Experiments with Di-tert-butyl diperoxyoxalate

Di-tert-butyl diperoxyoxalate does not provide chemiluminescence when decomposed in xylene in the presence of 9,10-diphenylanthracene or when combined with oxalyl chloride in ether.

(f) Effect of Other Oxidants

Tertiarybutylhydroperoxide, cyclohexanone peroxide, and benzoyl peroxide react with oxalyl chloride in anhydrous ether containing 9,10-diphenylanthracene, but little light is generated. Oxygen is also ineffective in providing chemiluminescence, but a peroxide derived from autooxidation of diethylether provides a moderate emission.

(g) Absence of Direct Interaction between the Acceptor and Either Reactant

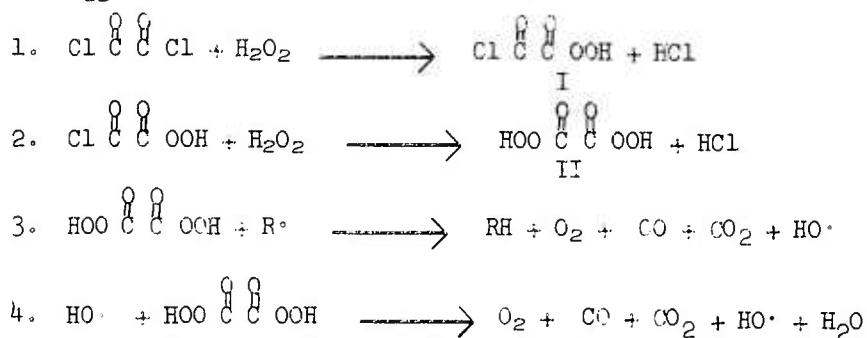
Ultraviolet spectral analyses of 9,10-diphenylanthracene mixtures with oxalyl chloride or with hydrogen peroxide indicate that no rapid interaction occurs in these systems.

(h) Stability of 9,10-diphenylanthracene under the Reaction Conditions

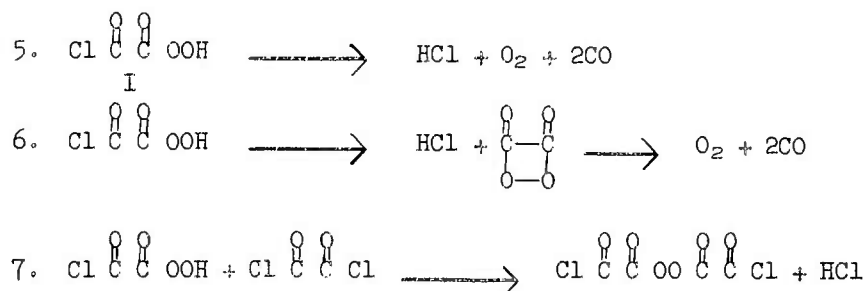
9,10-Diphenylanthracene is essentially unchanged in the presence of the oxalyl chloride-hydrogen peroxide reaction as indicated by fluorescence spectral analysis of a completed chemiluminescent reaction mixture.

Discussion

A tentative mechanism in agreement with the available information is suggested below.



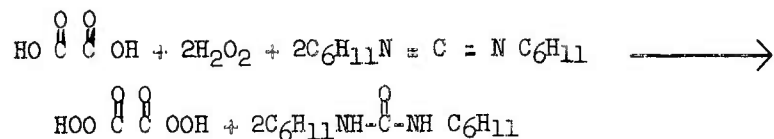
Equation (1) is the normal hydrolytic reaction expected initially between oxalyl chloride and hydrogen peroxide. The product monoperoxide acid chloride, I, might react with hydrogen peroxide according to equation (2) to give diperoxyoxalic acid, II, or alternatively undergo reactions (5) through (7) below.



While all of these reactions are theoretically possible under the conditions employed, reactions (5) through (7) are not free radical chain processes and should not be substantially affected by small amounts of free radical inhibitors (fact b). Moreover, reaction (7) would be facilitated by high oxalyl chloride concentrations, and under these conditions the quantum yield is very low (fact c).

Steps (3) and (4) represent a free radical chain decomposition process. Such a process is required by the observed quenching by free radical inhibitors (fact b) and is in agreement with the observed stoichiometry (fact d). Moreover, if a non-chain decomposition of II were involved, one would expect chemiluminescence from decompositions of di-tert-butyl diperoxyoxalate in the presence of 9,10-diphenylanthracene and this was not observed (fact e). The failure of organic peroxides to provide chemiluminescence on reaction with oxalyl chloride (fact f) also supports this view, although the positive result obtained from an ether-derived peroxide requires further study.

The mechanism proposed above assigns a key role to diperoxyoxalic acid, II. If the mechanism is valid, diperoxyoxalic acid prepared by alternative routes should generate light on decomposition in the presence of a fluorescent compound. To test this prediction, oxalic acid was reacted with anhydrous ethereal hydrogen peroxide in the presence of dicyclohexylcarbodiimide, a catalytic amount of methane sulfonic acid, and 9,10-diphenylanthracene. The powerful carbodiimide method for preparing peroxyacids<sup>4</sup> would be expected to provide II as an unstable intermediate.

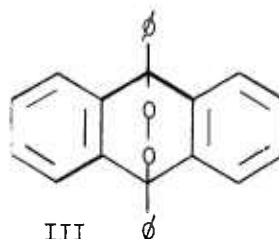


## II

The experiment as carried out in the dark generated a bright blue, although brief, chemiluminescent emission quite similar to that obtained from oxalyl chloride, hydrogen peroxide, and 9,10-diphenylanthracene. This new reaction will be investigated in more detail.

Thus a substantial body of data has been gathered in support of the proposed mechanism. Additional confirmatory evidence will be sought.

The mechanism of the key process by which the fluorescent acceptor is converted to its singlet excited state remains unresolved. Direct chemical involvement of 9,10-diphenylanthracene, a typical acceptor, with either oxalyl chloride or hydrogen peroxide has been ruled out (fact g), and we have shown (fact h) that this acceptor is not substantially consumed during a chemiluminescent reaction. Chemical reaction of the acceptor with an intermediate produced in the reaction followed by regeneration of the acceptor in a second step remains a possibility. This seems unlikely, however, because a variety of fluorescent compounds having differing structures has been shown to be active<sup>2</sup>, and a single reaction common to all is hard to imagine. Moreover, the most likely intermediate derived from a fluorescent anthracene would be a transannular peroxide such as III.



Such compounds are indeed known to generate chemiluminescence on decomposition and the starting anthracene is regenerated<sup>5</sup>. However, the temperatures required for such decompositions are on the order of 150° or higher<sup>5</sup>, and decomposition would not be expected under the conditions of the oxalyl chloride-hydrogen peroxide reaction. The possibility of chemical involvement of the acceptor thus seems remote, but will be explored further.

The alternative to chemical reaction of the acceptor with a reactive intermediate is a physical process of energy transfer. There are two general physical processes that might account for the generation of a singlet excited state of the acceptor. The first requires a transfer of singlet excitation energy by a collisional, non-resonance mechanism from an excited donor produced in the chemical reaction to the acceptor<sup>6</sup>. The second general mechanism requires a concerted process whereby energy is transferred simultaneously with decomposition of a chemical intermediate<sup>1</sup>. These various possibilities will be studied in future experiments.



B. Chemiluminescence from 3-Aminophthalhydrazide ("Luminol")

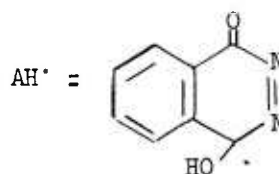
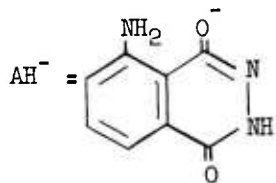
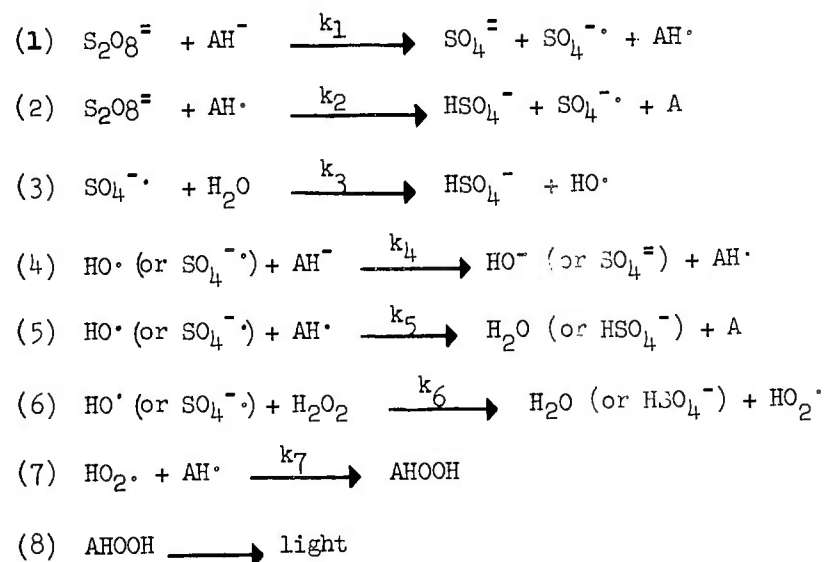
The best known and most efficient chemiluminescent systems now available are based on oxidations of 3-aminophthalhydrazide under alkaline conditions<sup>7</sup>. Strong intensities and moderate lifetimes can be obtained by oxidation with oxygen in strongly alkaline dimethylsulfoxide solution<sup>8</sup>, where the quantum yield has been reported to be on the order of ten per cent<sup>7i</sup>. Most investigators have studied oxidation in aqueous solution with hydrogen peroxide and a co-oxidant or catalyst such as potassium ferricyanide, sodium hypochlorite, or hemin. Under these conditions quantum yields on the order of 0.1% have been reported most frequently<sup>9</sup>. (A few investigators have reported higher values which must be considered doubtful in view of the disagreement<sup>10</sup>.)

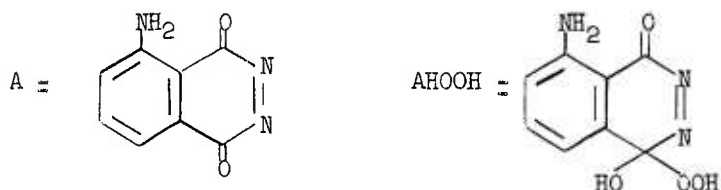
Prior to the commencement of work under this contract, it was discovered by Dr. J. M. W. Scott and Mr. R. Phillips in these laboratories, that the oxidation of 3-aminophthalhydrazide with potassium persulfate and hydrogen peroxide in aqueous alkaline solution provided unexpectedly high chemiluminescent intensities and long lifetimes<sup>11</sup>. This system was well suited for kinetic and quantum yield analyses, which were carried out at that time<sup>12</sup>. The mechanistically significant results of that investigation are summarized briefly below.

(1) In the presence of excess hydrogen peroxide the reaction is first order in 3-aminophthalhydrazide and first order in persulfate. (2) The reaction is essentially zero order in hydrogen peroxide except, perhaps,

at very low hydrogen peroxide concentrations. (3) The reaction is essentially zero order in base. (4) The quantum yield decreases only moderately with increasing 3-aminophthalhydrazide or persulfate concentrations. (5) The quantum yield increases substantially with increasing hydrogen peroxide concentrations.

The following mechanism, in agreement with these earlier observations and in agreement with results from other persulfate oxidation reactions<sup>13</sup> was tentatively suggested.





Many persulfate oxidation reactions are first order in persulfate but zero order in the oxidized material. Such first order reactions are believed to operate through an autocatalytic cyclic chain process involving steps (2), (3) and (4) and initiated by the slow step (9).<sup>13</sup>



Application of the steady state approximation to the autocatalytic mechanism provided the required first order rate law. In the chemiluminescent reaction, however, the kinetics were first order in the oxidized material as well as first order in persulfate. We suggested that step (1) is rate determining, and that steps (2) and (4) are inhibited by hydrogen peroxide acting in steps (6) and (7). Thus hydrogen peroxide decreases the steady state concentrations of intermediates  $[^{\cdot-}HO^{\cdot-}]$  and  $[^{\cdot-}AH^{\cdot-}]$ , reducing the importance of steps (2) and (4) relative to step (1). Other steps commonly proposed for persulfate and hydrogen peroxide oxidations such as (10) and (11) would not be expected to affect the reaction rate.



The important effect of hydrogen peroxide on the quantum yield would stem from steps (6) and (7) which we suggested were essential

for the generation of light. The key radical  $AH^\bullet$  can react with persulfate in step (2) and the fraction of  $AH^\bullet$  that is diverted to  $AHOOH$  will depend on the peroxide concentration. This does not affect the over-all rate of reaction, however, which is determined by step (1).

While this mechanism was in good agreement with the kinetic and quantum yield results and could easily be modified to account for chemiluminescence under other conditions, additional experimentation was desirable to provide confirmatory evidence. These experiments are currently underway and the results to date are summarized below.

(a) Effect of ethylenediaminetetraacetic acid

The trace amounts of copper present in reagent potassium persulfate (as was used in the previous kinetic work) have been shown to profoundly increase the rate of persulfate oxidations involving hydroperoxy intermediates by inducing hydroperoxide decomposition<sup>14</sup>. The above chemiluminescence mechanism, however, predicts the absence of such catalytic effects since hydroperoxide intermediates are not involved in the rate determining step. Since it has been shown that ethylenediaminetetraacetic acid eliminates such trace metal catalysis<sup>14</sup>, one of the earlier kinetic experiments was repeated in the absence and in the presence of ethylenediaminetetraacetic acid. The results are summarized in the following table. (The experimental procedure, which requires light intensity measurement, is described in Section III.)

Effect of EDTA on the Reaction of 3-Aminophthalhydrazide  
with  $K_2S_2O_8$  and  $H_2O_2^a$

Conc. of EDTA (moles per liter)	Second Order Rate Constant (liters mole <sup>-1</sup> sec <sup>-1</sup> )	Quantum Yield
none <sup>b</sup>	$1.5 \times 10^{-2}$	c
none	$1.4 \times 10^{-2}$	0.92%
$1.0 \times 10^{-4}$ M	$1.2 \times 10^{-2}$	0.98%

(a) The three experiments were carried out with  $4 \times 10^{-3}$  molar 3-aminophthalhydrazide,  $6 \times 10^{-2}$  molar  $K_2S_2O_8$ , and  $3 \times 10^{-2}$  molar  $H_2O_2$  in 0.10M aqueous potassium carbonate solution at 29.0°.

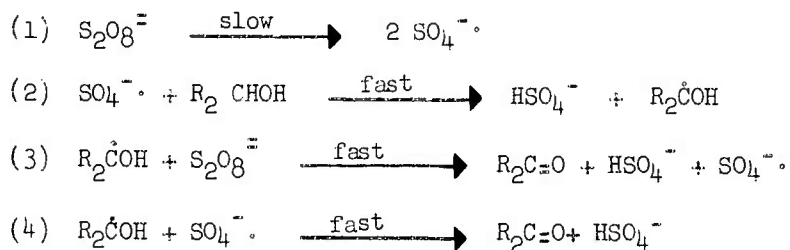
(b) Result from earlier work at 29.29°.

(c) Not determined on an absolute basis.

It is clear from the table that trace metal catalysis is not a factor influencing rates or quantum yields in 3-aminophthalhydrazide-persulfate-peroxide chemiluminescence.

(b) Effect of allyl acetate

The oxidation of isopropyl alcohol to acetone by persulfate is believed to proceed according to the following mechanism<sup>14</sup>.



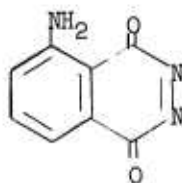
Since the propagation step (1) is slow, the over-all rate is determined by the autocatalytic steps (2) and (3), and by the termination step (4).

The addition of allyl acetate drastically reduces the rate of this reaction by trapping the  $\text{SO}_4^{\cdot -}$  ion radical (or the kinetically equivalent  $\cdot\text{OH}$  radical and blocking step (2)<sup>14,15</sup>. If such an autocatalytic process determined the rate of the 3-aminophthalhydrazide-persulfate-hydrogen peroxide reaction, one would expect allyl acetate to produce a similar decrease in kinetic rate and chemiluminescent intensity.

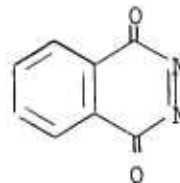
We find, however, that  $2.0 \times 10^{-3}$  molar allyl acetate has no substantial effect on either the intensity or the lifetime of the 3-aminophthalhydrazide-persulfate-hydrogen peroxide reaction. This result rules out participation by the sulfate ion radical or by the hydroxyl radical in the rate determining step and is in agreement with the above chemiluminescence mechanism.

(c) The effect of dienes

None of the evidence presented above conclusively rules out participation of the azoquinone I in the chemiluminescence mechanism.



I

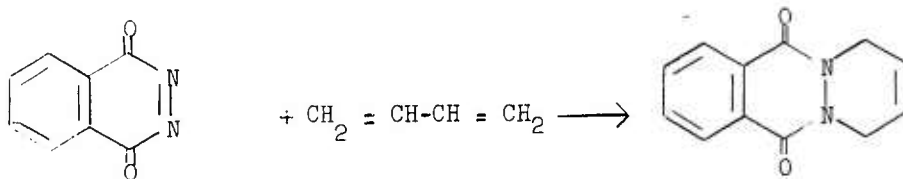


II

The azoquinone would be the product of a two-electron oxidation of 3-aminophthalhydrazide and might react with hydrogen peroxide to ultimately produce chemiluminescence. Such a mechanism would in general be

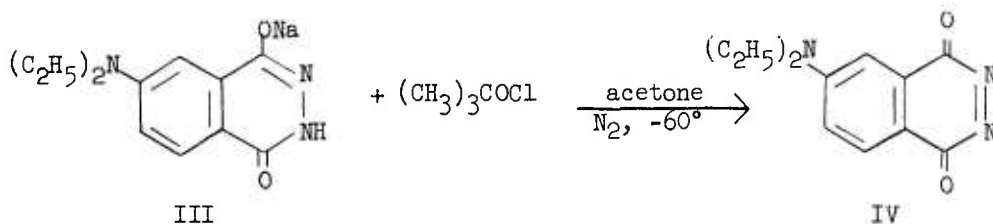
consistent with a mechanism proposed for the persulfate oxidation of phenols<sup>16</sup>. Two approaches are being taken to resolve this possibility.

(1) 1,4-Phthalazinedione, II, has been described in the literature and some of its properties are known<sup>17,18</sup>. Although it is unstable at room temperature, it is a highly active dieneophile and can be trapped efficiently by reaction with such dienes as 1,3-butadiene and N-methylpyrrole<sup>17,18</sup>.

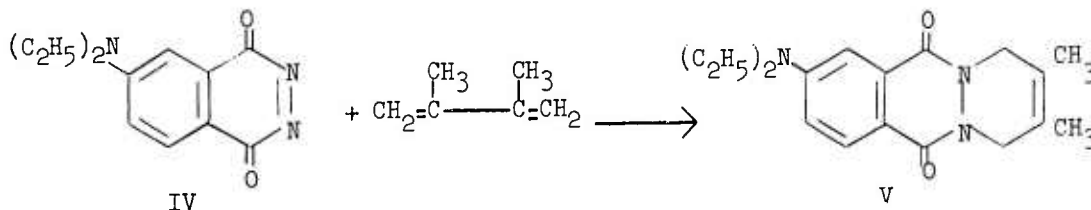


Since the azoquinone I would be expected to have similar properties, dienes should serve as effective trapping agents. Thus if I were an intermediate in 3-aminophthalhydrazide chemiluminescent oxidations, one would expect the addition of a diene to quench the luminescence by blocking subsequent reaction of I with oxygen or hydrogen peroxide. To investigate this point substantial concentrations of 1,3-butadiene or N-methylpyrrole were added to chemiluminescent oxidations of 3-aminophthalhydrazide with oxygen in alkaline *N,N*-dimethylformamide solution. In neither experiment was any decrease in intensity observed, indicating that I is probably not involved in the chemiluminescence process.

(2) A more direct and unequivocal evaluation of this point might be obtained by preparing an azoquinone in the absence of oxygen and determining its chemiluminescent properties on subsequent oxidation. As a first step in this direction we have attempted to apply a preparative method for II<sup>18</sup> to the synthesis of IV, the potential azoquinone intermediate in the strong chemiluminescence from 4-diethylamino-phthalhydrazide, III.



To substantiate the formation of IV, the reaction mixture was treated with 2,3-dimethyl-1,3-butadiene and an attempt was made to isolate the adduct V.



While addition of the diene produced a marked color change, indicating that a reaction took place, the product mixture obtained was complex, and attempts to isolate V by crystallization or chromatography were unsuccessful. Since this is a key mechanistic point, an additional effort will be made.



(d) The quantum yield of the aqueous 3-aminophthalhydrazide-potassium persulfate-hydrogen peroxide reaction

The quantum yield of this reaction has now been measured on an absolute basis. The reproducible value obtained was 0.95% (see Section IV). This value is substantially higher than values reported for other aqueous chemiluminescent systems<sup>9</sup>, but is still far short of the efficiency desired for a broadly practical system.

(e) Electroanalytical and electron spin resonance investigation of 3-aminophthalhydrazide oxidation

(1) Cyclovoltammetric Studies

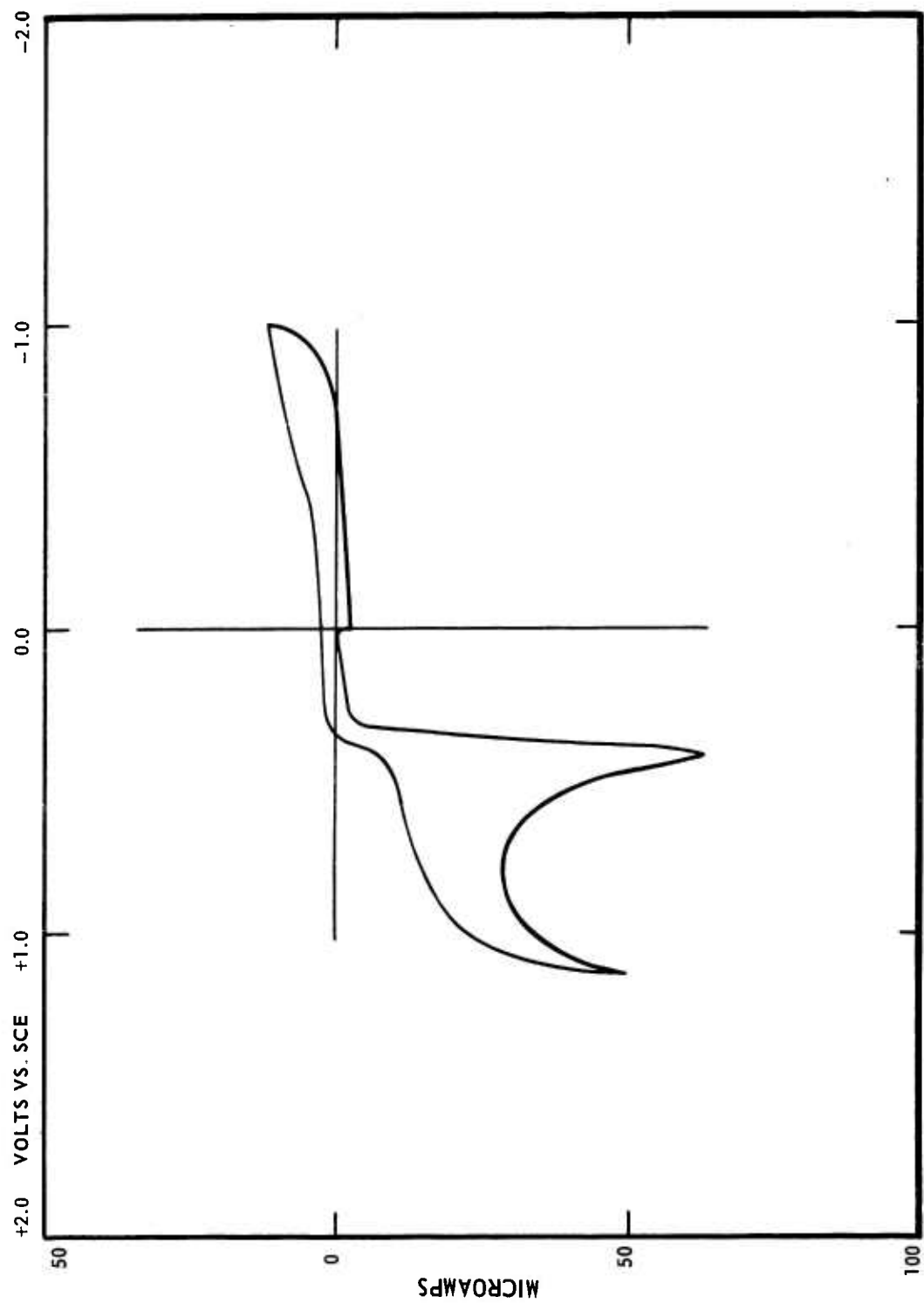
The electroanalytical technique of cyclic voltammetry has been applied to various 3-aminophthalhydrazide and phthalhydrazide systems in an effort to detect and investigate the short-lived intermediates produced on oxidation. The technique involves rapidly scanning the potential of a stationary electrode back and forth over the region of potential where reactions of interest occur and recording the current as a function of potential. At the potential where oxidation or reduction takes place a sharp increase in current is observed which characterizes the reaction and denotes the formation of a specific oxidation or reduction product. Since the sweep time is rapid, short-lived oxidation intermediates can often be detected on the return sweep where reduction to the original starting material is observed at a specific potential. The current measured at such a potential is dependent on the concentration of the intermediate; thus by varying the scan rate, the lifetimes of such intermediates can be

measured.

Figures 1 and 2 picture the cyclic voltammograms of the monoanions of 3-aminophthalhydrazide and phthalhydrazide obtained with a carbon paste electrode in a nitrogen purged aqueous pH 11 carbonate buffer. 3-Aminophthalhydrazide is seen to undergo two separate oxidation reactions at +0.4 V and +0.9 V vs. the saturated calomel electrode, while phthalhydrazide exhibits only the first oxidation at +0.4 V. Clearly the phthalhydrazide ring oxidizes at +0.4 V and the amino function at +0.9 V. Chemiluminescence is observed beginning at +0.4 V when this system is oxygenated. Thus it is clear that oxidation of the phthalhydrazide ring provides the primary intermediate in the chemiluminescence process and that this or a subsequent intermediate must then react with oxygen or a related radical to generate light. Moreover, since further oxidation can occur at higher potential with 3-aminophthalhydrazide, loss in chemiluminescent efficiency would be expected with oxidizing agents having oxidation potentials above  $\sim +0.7$  V.

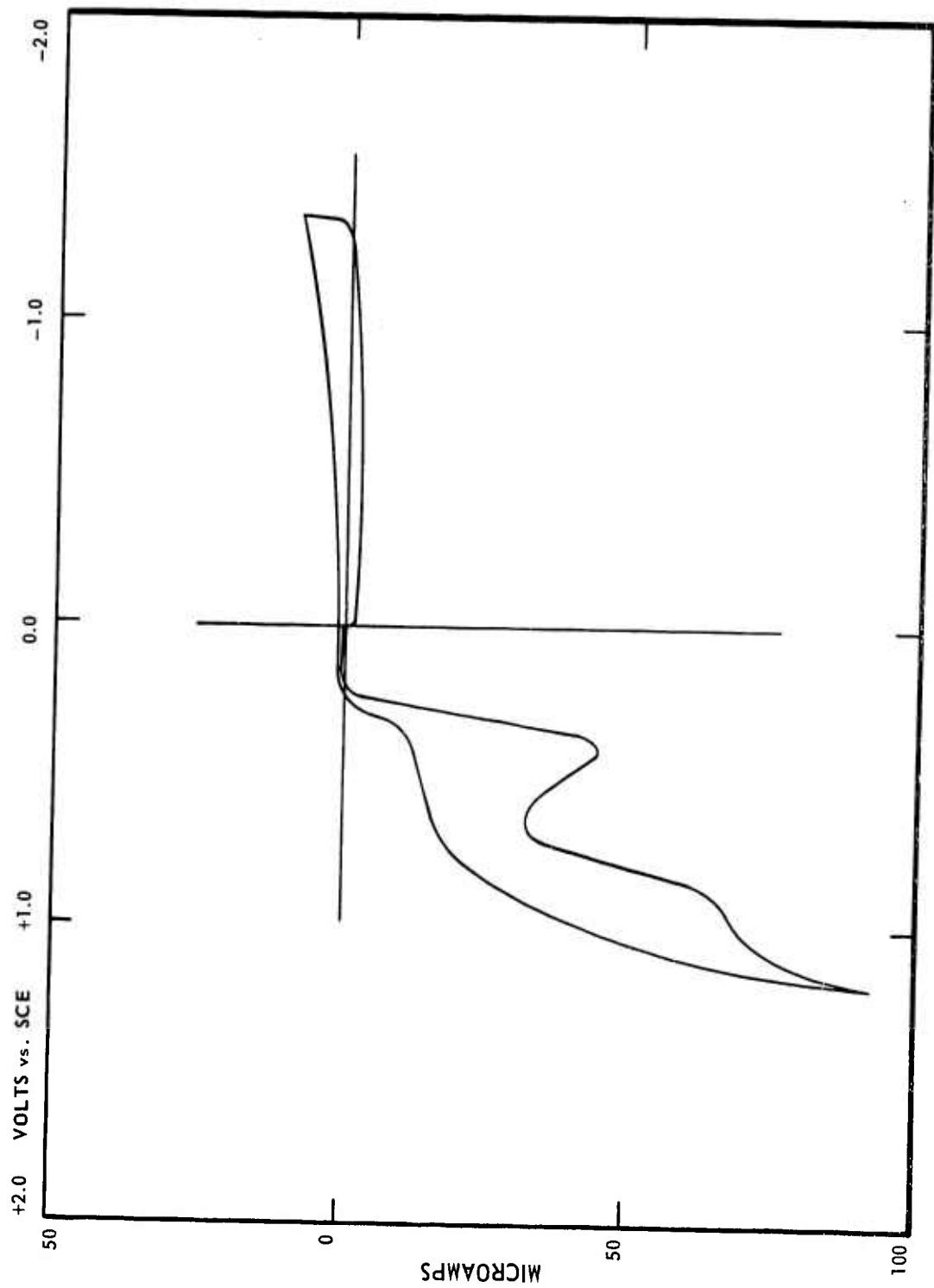
As evident from Figures 1 and 2, none of the oxidation products of either compound are stable under the conditions used. Indeed by scanning over the first 3-aminophthalhydrazide peak at high rates, it was estimated that the lifetime of the product was less than 65 milliseconds. This is in agreement with the coulometric data of Kuwana<sup>19</sup> which indicated a half life of  $6.8 \pm 0.2$  milliseconds in 0.1 M  $\text{Na}_2\text{CO}_3$ .

FIGURE 1  
CYCLICVOLTAMMAGRAM OF PHTHALHYDRAZIDE



pH 11 CARBONATE BUFFER CARBON PASTE ELECTRODE SCAN RATE 83 mv/sec.

FIGURE 2  
CYCLICVOLTAMMAGRAM OF 3-AMINOPHTHALHYDRAZIDE



pH 11 CARBONATE BUFFER CARBON PASTE ELECTRODE SCAN RATE 83 mv/sec.

The stability of the initial oxidation products of both 3-aminophthalhydrazide and phthalhydrazide increases with decreasing pH. Estimated lifetimes of the primary oxidation products under varying conditions are summarized in Table I. While these estimates are only approximate because of film formation on the electrode, the gross effects of pH are evident. While the influence of pH is not yet completely understood, this result is in agreement with quantum yield measurements which demonstrate that chemiluminescent efficiency decreases drastically at higher alkalinity<sup>12</sup>. Moreover, it is clear that the hydroxyl ion facilitates decomposition of the initial intermediate, perhaps by an acid-base neutralization process.

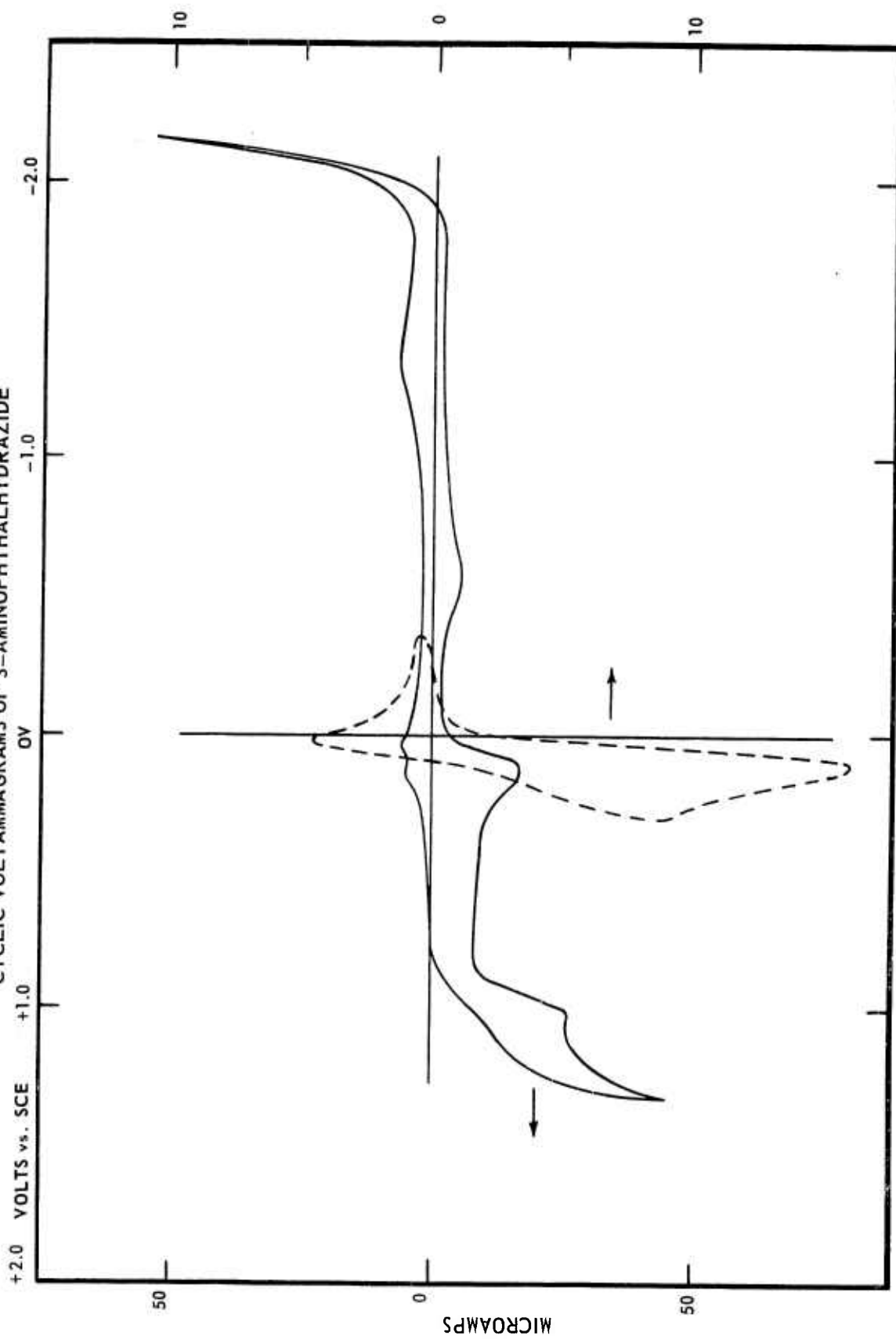
The cyclic voltammetry of the two phthalhydrazides was also investigated in a variety of non-aqueous solvents as indicated in Table I. A typical curve for the monotetrabutylammonium salt of 3-aminophthalhydrazide in dimethylsulfoxide (DMSO) is shown in Figure 3. Again two oxidation peaks are present at +0.1 V and +1.0 V, respectively. Two re-reduction peaks are also apparent at +0.15 V and +0.03 V. The peak at +0.15 V is seen only after the aminooxidation peak (1.0 V) has been scanned and is therefore due to a decomposition product of this oxidation. The re-reduction at +0.03 is characteristic of the initial oxidation product formed at +0.1 V. An electrochemically irreversible reduction and reoxidation is also apparent at about -1.3 and -0.5 V, respectively. The voltammograms are similar in the other non-aqueous solvents used. However, as shown in Table I the stability of the

TABLE I

The Lifetime of Phthalhydrazide Oxidation Products as a Function of Solvent and pH

Compound	Solution	Lifetime of Oxidation Products	
		Cyclic Volt.	e.s.r.
3-aminophthalhydrazide	aqueous phosphate-borax buffers pH 7	0.5 sec.	-
"	" " " pH 8	0.4 sec.	-
"	" " " pH 9	0.7 sec.	No signal detected
"	" " " pH 10	0.1 sec.	-
"	aqueous carbonate buffer pH 11	<0.065 sec.	No signal detected
tetra-n-butylammonium 3-aminophthalhydrazide	0.1M (Bu) <sub>4</sub> NClO <sub>4</sub> in DMF	-	90 sec.
Na <sup>+</sup> 3-aminophthalhydrazide	0.1M (Bu) <sub>4</sub> NBr in DMF	10 sec.	-
tetra-n-butylammonium 3-aminophthalhydrazide	0.1M (Bu) <sub>4</sub> NClO <sub>4</sub> in 50-50 DMF-acetone	20 sec.	-
"	0.1M (Bu) <sub>4</sub> NClO <sub>4</sub> in DMSO	30 sec.	140 sec.
"	0.1M (Bu) <sub>4</sub> NClO <sub>4</sub> + 0.01 M (CH <sub>3</sub> ) <sub>3</sub> COK in DMSO	0.3 sec.	< 5 sec.
phthalhydrazide	aqueous phosphate-borax buffers pH 7	0.6 sec.	-
"	" " " pH 8	0.2 sec.	-
"	" " " pH 9	<0.06 sec.	-
"	0.1M (Bu) <sub>4</sub> NClO <sub>4</sub> + equivalent amt. (CH <sub>3</sub> ) <sub>3</sub> COK in DMF	-	10 sec.
"	0.1M (Bu) <sub>4</sub> NClO <sub>4</sub> + equivalent amt. (CH <sub>3</sub> ) <sub>3</sub> COK in 50-50 DMF-acetone	9 sec.	-

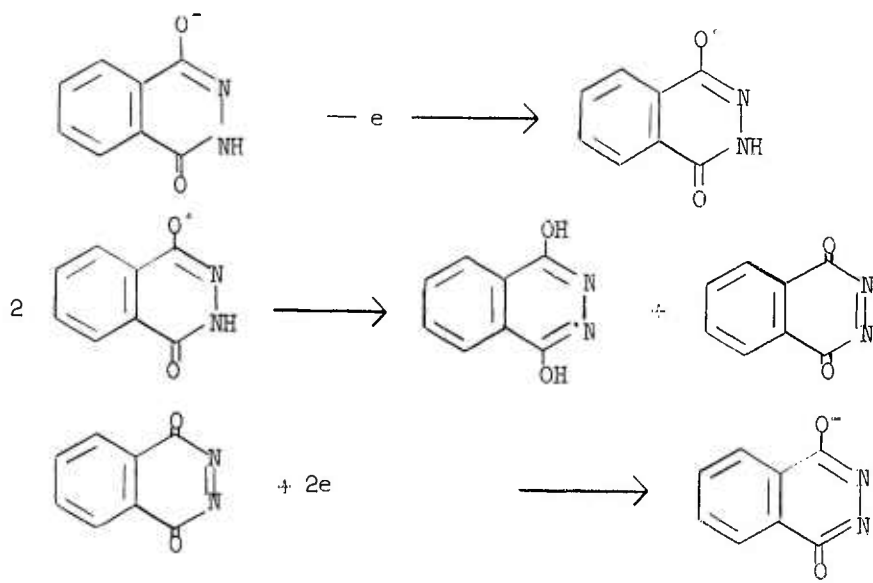
FIGURE 3  
CYCLIC VOLTAMMAGRAMS OF 3-AMINOPHTHALHYDRAZIDE



0.1M (Bu)<sub>4</sub>NClO<sub>4</sub> IN DMSO PLATINUM ELECTRODE SCAN RATE 83 mv/sec.

oxidation products derived from the monoanions of 3-aminophthalhydrazide and phthalhydrazide is about an order of magnitude greater in the non-aqueous solvents.

An attempt was made to measure the stability of the initial oxidation product from the 3-aminophthalhydrazide monoanion at  $-78^{\circ}$  in an acetone-dimethylformamide mixture. However, the oxidation was irreversible under these conditions and no reliable estimate could be made. The monoanion of phthalhydrazide did oxidize reversibly under these conditions to give a well defined peak at  $+0.27$  V. A re-reduction peak was observed at  $-1.18$  V, which clearly did not correspond to the initial oxidation product. This species observed on re-reduction was necessarily derived from the initial oxidation product, however, and was evidently stable under the reaction conditions. Since 1,4-phthalazine dione is known to be stable at  $-78^{\circ}$ <sup>17,18</sup> the following equations provide a reasonable representation of the process.





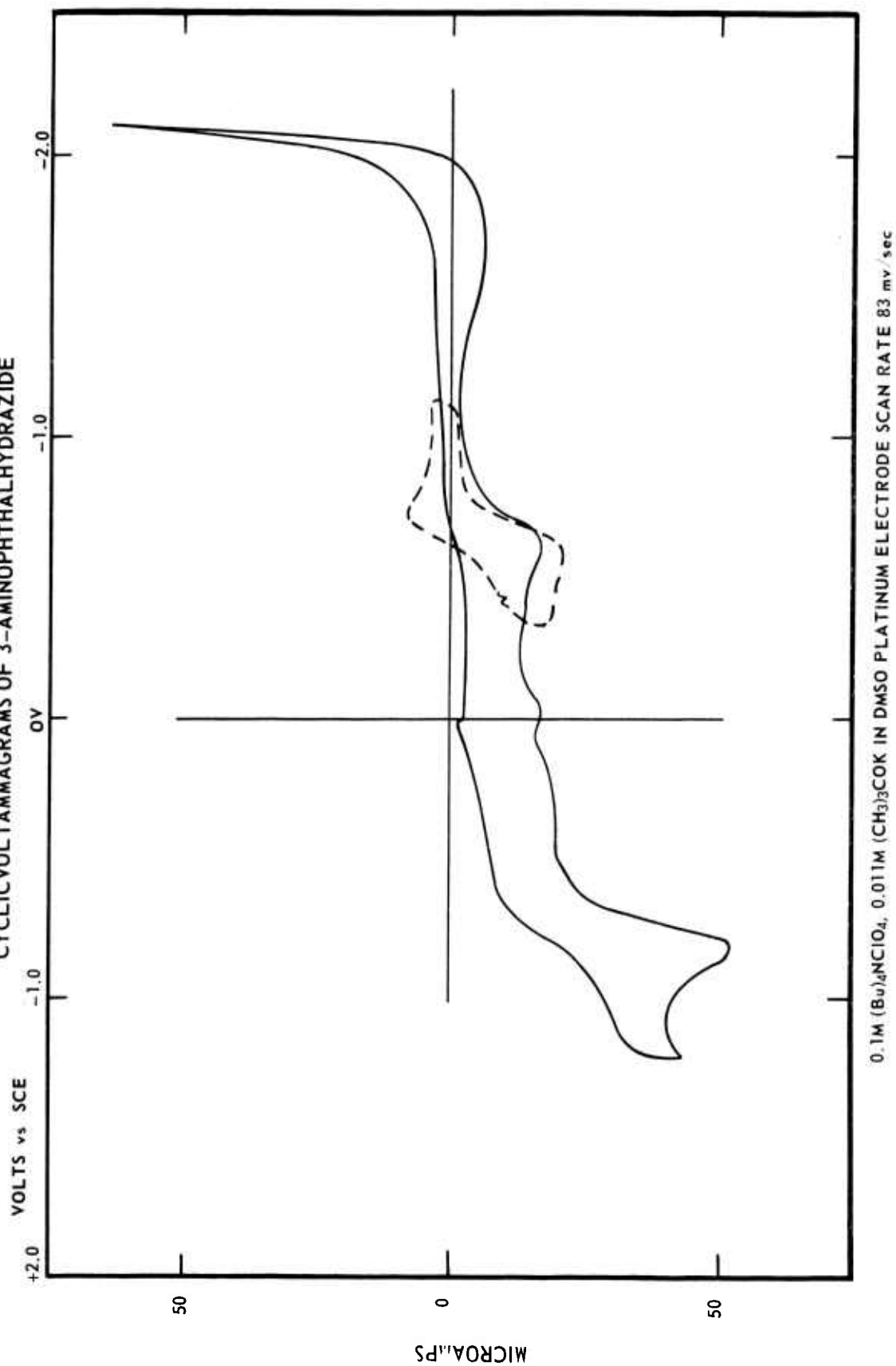
A critical question regarding the initial oxidation step of 3-aminophthalhydrazide monoanion is whether the process involves a one or two electron change. Attempts were made to measure this "n" value by means of a rotating carbon paste electrode in an aqueous buffer solution at pH 11 and with rotating platinum or dropping mercury electrodes in dimethylformamide solution. Varying values ranging from less than 1 to about 2 were obtained, however, and a reliable answer could not be obtained.

A cyclic voltammetric measurement of 3-aminophthalhydrazide oxidation in strongly alkaline dimethylsulfoxide is pictured in Figure 4. 3-Aminophthalhydrazide exists as the easily oxidized dianion under such conditions, and as expected the oxidation peak corresponding to the initial product shifted to -0.6 V. The lifetime of this intermediate is only 0.3 seconds under these conditions, but it may, nevertheless, be possible in future experiments to measure the rate of its reaction with oxygen.

## (2) E.S.R. Results

One of the most powerful arguments for a one electron product of an electrochemical process is the detection of a radical as an initial product. Starting with a diamagnetic molecule, a radical can be produced only by the removal or addition of an odd number of electrons. Furthermore, in many cases the e.s.r. spectra positively identifies the species involved. Therefore, electrolytic oxidations of 3-aminophthalhydrazide and phthalhydrazide were carried out in the cavity of the e.s.r. spectrometer.

FIGURE 4  
CYCLICVOLTAMMAGRAMS OF 3-AMINOPHTHALHYDRAZIDE



A comparatively simple spectrum was produced by the oxidation of both 3-aminophthalhydrazide and phthalhydrazide, as shown in Figure 5, although the radical lifetime changed with the solvent as seen in Table II. Because of the instability of the radical, there was often asymmetry in the spectrum due to the change of radical concentration in the time required to trace a spectrum. However, under conditions where longer lived radicals were observed, the 1:2:3:2:1 ratio of the intensities of the e.s.r. lines could be established, and in all other cases the intensities of neighboring lines were in good agreement with this intensity relationship.

The fast decay of the radicals in certain solvents prevented measurements being taken to analyze the kinetics of decay. However, in dimethylformamide solution measurements could be made but did not fit either a first or second order kinetic process. In dimethylsulfoxide solution, on the other hand, decay down to the 10% level fit a second order plot quite well.

The comparison of the lifetimes of the oxidation products of both the mono and the dianion of 3-aminophthalhydrazide and the monoanion of phthalhydrazide with the lifetime of the radical observed by e.s.r. spectrometry is shown in Table I. The agreement is considered to be reasonable. Although several of the e.s.r. measured lifetimes are greater by a factor of 4 or 5, this may well be an experimental artifact due to the filming difficulties encountered in the cyclic voltammetric measurements. This leaves little doubt that the species

FIGURE 5  
MONOTETRABUTYLAMMONIUM 3-AMINOPHTHALHYDRAZIDE IN DIMETHYLFORMAMIDE  
OXIDIZED "IN SITU" IN E.S.R. CAVITY

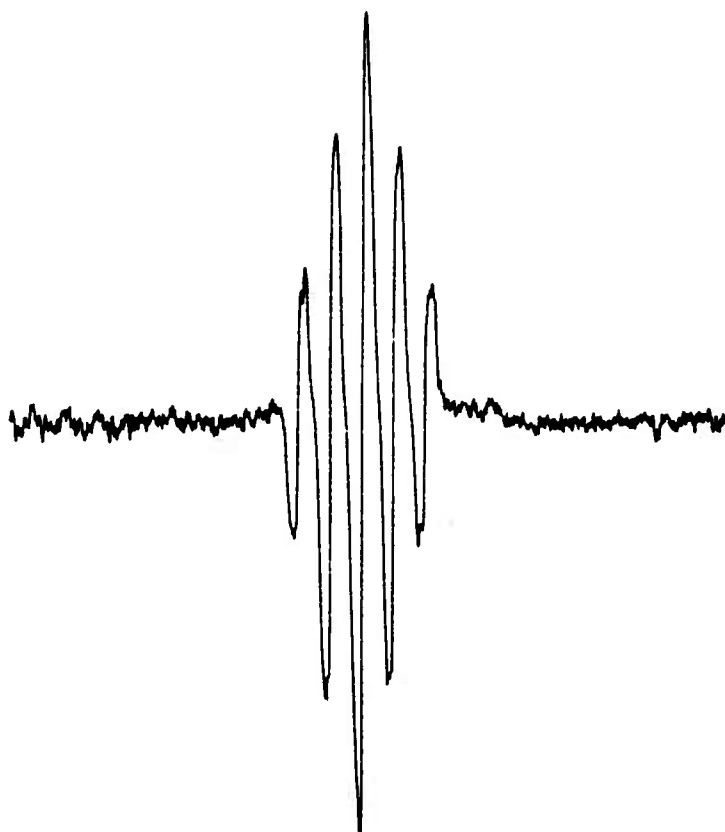


TABLE II  
Electron Spin Resonance Data

Molecule	Solvent	Spectrum	Hyperfine Coupling Constant in Gauss	Line Width in Gauss	Nature of Decay
Monoanion of 3-amino-phthalhydrazide	water at pH 9	No spectrum	-	-	-
Monoanion of 3-amino-phthalhydrazide	DMF	5 lines; Ratio 1:2:3:2:1	$3.84 \pm 0.05$	1.6	Not 1st or 2nd Order Decayed to 10% in 90 sec.
Monoanion of 3-amino-phthalhydrazide	DMSO	5 lines; Ratio 1:2:3:2:1	$3.81 \pm 0.05$	1.85	2nd Order Decayed to 10% in 140 sec.
Dianion of 3-amino-phthalhydrazide	DMSO + base	5 lines; Ratio 1:2:3:2:1	$3.90 \pm 0.10$	2.0	Decayed to 10% in 5 sec.
Monoanion of phthalhydrazide	DMF	5 lines; Ratio 1:2:3:2:1	$3.78 \pm 0.05$	1.4	Decayed to 10% in 10 sec.

responsible for the re-reduction peak, and the radical observed by the e.s.r. are one and the same species. Thus it has been established that the primary product of 3-aminophthalhydrazide is a radical, evidently resulting from a one-electron oxidation.

The intensities of 1:2:3:2:1 can only arise from the interaction of the unpaired electron with two equivalent nitrogen atoms. The observation of a very similar spectrum from oxidized phthalhydrazide shows that the nitrogens concerned are those in the heterocyclic ring. Furthermore, since the hyperfine coupling constant to the nitrogens is the same (within experimental error, in 3-aminophthalhydrazide and phthalhydrazide there can be very little of the unpaired electron spin density on the benzene ring. This hypothesis receives support from the failure to observe hyperfine splittings from protons on the benzene ring. Any hyperfine interaction with these protons must therefore be smaller than the narrowest observed line width (1.4 gauss in phthalhydrazide).

The e.s.r. spectrum is thus in excellent agreement with the structure proposed for the initial intermediate  $\cdot\text{AH}$  in the mechanism described earlier.

The kinetic measurements are sufficient to exclude spontaneous instability of the radical as its mode of decomposition, since this should fit first order kinetics. For higher orders of reaction the measurements are complicated by the existence of a non-uniform concentration of radicals over the electrode and are further complicated by a non-uniform e.s.r. sensitivity over this region. The lack of

agreement with a second order plot cannot therefore be taken as excluding a second order mode of decay.

The over-all electroanalytical and electron spin resonance results presented above agree well with the proposed chemiluminescence reaction mechanism, indicating that a free radical generated by a one electron oxidation process reacts with oxygen to produce an intermediate (presumably a hydroperoxide) which reacts further to produce chemiluminescence. Additional effort will be made to further confirm this critical conclusion.

Comparison of the results obtained from 3-aminophthalhydrazide oxidations with those obtained from phthalhydrazide oxidations demonstrates that the initial chemical processes involved are identical. Thus it would appear that the lack of chemiluminescence from phthalhydrazide results from the poor fluorescence efficiency of the emitting species, rather than from a difference in chemistry.

## SECTION I

### EXPERIMENTAL

#### Effect of Free Radical Inhibitors

To a brightly glowing solution prepared from 10.0 ml. (1.0 mmole) of 0.1 molar oxalyl chloride in ether, 10.0 ml. (1.0 mmole) of 0.1 molar anhydrous hydrogen peroxide in ether, and 5 mg. of 9,10-diphenylanthracene was added 1.0 ml. (0.1 mmole) of a 0.1 molar solution of 2,6-ditertiary butyl cresol in ether. The intensity of the reaction was reduced at once to a very low level. In similar experiments butyl sulfide, hydroquinone, and dilaurylthiodipropionate also had very substantial quenching effects.

#### Reaction Conditions and Stoichiometry

##### Method A

An apparatus consisting of a magnetically stirred 150 ml. three-necked flask fitted with a 50 ml. buret and attached to a constant pressure nitrogen manifold was flushed well with nitrogen and charged with 10.0 ml. (1.020 mmoles) of 0.102 molar hydrogen peroxide in anhydrous diethyl ether and 5 mg. of 9,10-diphenylanthracene (DPA). The buret, also attached to the manifold, was then filled with 0.075 molar oxalyl chloride solution in anhydrous diethyl ether, and the entire assembly placed under a slight positive nitrogen pressure. Oxalyl chloride was added in 1.0 to 0.5 ml. portions. The chemiluminescence was allowed to decay to zero intensity between additions. The end point was reached when further addition failed to produce light and occurred at 16.0 ml. (1.200 mmoles) of oxalyl chloride solution. This is a ratio of 1.18 moles oxalyl chloride per mole of hydrogen peroxide. Until very near the end point, each addition of oxalyl chloride solution produced a bright chemiluminescent emission which required in excess of ten minutes to decay.

##### Method B

This experiment was similar to Method A except that the standard ethereal anhydrous hydrogen peroxide was added to the standard oxalyl chloride solution. A ratio of 0.94 moles of oxalyl chloride per mole of hydrogen peroxide was found.

Near the start of the titration the 1.0 ml. aliquotes of hydrogen peroxide solution produced dim and very brief chemiluminescent emissions. However, as the end point was approached and the oxalyl chloride concentration diminished, each addition produced much brighter and longer lived emission.



When 0.145 molar hydrogen peroxide in anhydrous 1,2-dimethoxy ethane was titrated with 0.094 molar oxalyl chloride in 1,2-dimethoxy ethane by this method a ratio of 1.17 moles of oxalyl chloride per mole of hydrogen peroxide was observed.

#### Experiments with Di-T-butyl Diperoxyoxalate

A solution of 1 g. of peroxyester, and about 5 mg. of 9,10-diphenylanthracene in about 100 ml. of xylene was heated gradually to 100°. Chemiluminescence was not observed.

Addition of oxalyl chloride to an ethereal solution of the peroxyester containing 9,10-diphenylanthracene failed to produce chemiluminescence.

#### Oxalyl Chloride-Hydroperoxide Chemiluminescence

I. A freshly prepared solution of 10 ml. of 1M oxalyl chloride in ether and 5 mg. 9,10-diphenylanthracene (DPA) was treated with 10 drops of tertiary butyl hydroperoxide in the dark. No chemiluminescence was noted.

II. A freshly prepared 1M solution of 10 ml. oxalyl chloride in ether and 5 mg. DPA gave a weak chemiluminescence when treated with 0.5 g. cyclohexanone peroxide in the dark.

III. A 1M solution of oxalyl chloride was added dropwise to 10 ml. of a solution of 5 mg. DPA in ether which had been aged 72 hours under oxygen. A weak blue chemiluminescence was observed.

#### Investigation of a Possible Interaction of Oxalyl Chloride and 9,10-Diphenylanthracene

The ultra-violet absorption spectrum of an approximately  $1 \times 10^{-5}$  M solution of 9,10-diphenylanthracene in ether was run on a Bausch and Lomb Spectronic 505 spectrophotometer. Absorption bands at 216, 260, 337, 355, 373, and 393 millimicrons were observed. The ultra-violet spectrum of an identical solution which in addition contained  $2 \times 10^{-2}$  M oxalyl chloride did not differ in any respect indicating a lack of any interaction.

#### Diperoxyoxalic Acid

I. A slurry of 0.45 g. (0.005 mole) of powdered oxalic acid and 5 mg. of 9,10-diphenylanthracene in 2 ml. of methane sulfonic acid was cooled to 0°C. and 0.57 g. (0.015 mole) of 90% hydrogen peroxide added dropwise in the dark. No chemiluminescence was observed. Addition

of the peroxide required 5 min. and resulted in a clear solution. The reaction mixture was maintained at 0° for one hour. Vigorous evolution of gas occurred when the solution was allowed to warm, but again no chemiluminescence was observed.

II. A mixture of 0.5 g. (0.0056 mole) of powdered oxalic acid, 5 drops of methane sulfonic acid and 5 mg. of 9,10-diphenylanthracene in 25 ml. (0.025 mole) of 1 molar anhydrous hydrogen peroxide in ether was treated with a solution of 2.29 g. (0.011 mole) of dicyclohexylcarbodiimide in 10 ml. of ether in the dark. A bright brief blue chemiluminescence was observed. When the experiment was repeated without methane sulfonic acid, the light intensity was much lower but still clearly evident.

#### Effect of Allyl Acetate on Aqueous 3-Aminophthalhydrazide Chemiluminescence

A chemiluminescent solution which was  $4.0 \times 10^{-3}$  molar sodium 3-aminophthalhydrazide,  $6.0 \times 10^{-2}$  molar potassium persulfate,  $3.0 \times 10^{-2}$  molar hydrogen peroxide,  $1.0 \times 10^{-1}$  molar potassium carbonate and  $1.0 \times 10^{-1}$  molar in allyl acetate was compared to a control mixed simultaneously and lacking allyl acetate. No difference in the intensity or lifetime of the solutions was observed.

#### Effect of 1,3-Butadiene on 3-Aminophthalhydrazide Chemiluminescence

A solution of 4.43 g. (0.025 mole) of 3-aminophthalhydrazide in 100 ml. of N,N-dimethylformamide was combined with a solution of 25 ml. (0.125 mole) of 5.0 molar hydrogen peroxide in N,N-dimethylformamide, and the mixture was cooled to 0°C. and reacted with 10 ml. of 50% aqueous potassium hydroxide. A bright blue chemiluminescence was produced. Addition of 11.0 g. (0.2 moles) 1,3-butadiene had no effect on the chemiluminescence.

#### Attempted Preparation of 6-Diethylamino-1,4-Phthalazinedione Diels-Alder Adduct with 2,3-Dimethylbutadiene

A solution of 1.19 g. (0.011 mole) of tertiarybutyl hypochlorite in 15 ml. of acetone precooled to -55 to -60° C. was added to a suspension of 2.55 g. (0.01 mole) of the sodium salt of 4-diethylaminophthalhydrazide in 15 ml. of acetone at -55 to -60° under nitrogen. An intense red-violet color was produced instantaneously. After 6 hours at -55 to -60°, 1.64 g. (0.02 mole) 2,3-dimethyl-1,3-butadiene was added to the reaction and the temperature allowed to rise. On reaching -20° the color of the solution changed to a pale yellow brown. The reaction was filtered at room temperature to yield 0.10 g. (4%) of unchanged sodium 4-diethylamino phthalhydrazide. Evaporation

of the filtrate gave a yellow oil which on dissolving in chloroform and treatment with hexane gave 1.1 g. of a yellow solid m.p. 90-160°. Infrared spectra showed anhydride and N-H components were present in the solid. Fractional crystallization of the solid with benzene-hexane failed to give pure material. Chromatography of the largest (0.3 g.) fraction on a 2.5 x 25 cm neutral alumina column also failed to give a pure product.

#### Cyclic Voltammetry Measurements

The cyclic voltammetry was carried out using an operational amplifier based 3-electrode polarograph similar in design to that described by Smith<sup>20</sup>. The triangular voltage wave form was obtained from a Hewlett Packard Model 202A low frequency function generator. Voltammograms were recorded on a Moseley Autograf Model 35 X-Y recorder or a Hewlett Packard Model 130B oscilloscope equipped with a Polaroid camera. A 3-electrode cell of conventional polarographic design was employed.

The apparatus used for the in situ e.s.r. generations was constructed from a commercial Varian 0.5 mm. quartz cell designed for aqueous solution by attaching liter flasks by means of glass tubing and T fittings to the top and bottom of the cell. The solution was placed in the lower flask, purged with prepurified nitrogen and then pumped by nitrogen pressure to the upper flask. Fresh portions of this solution could then be introduced into the cell by siphon action. In this way a depleted solution could be renewed, and any stable paramagnetic species could be swept from the cell. A platinum gauze served as a generating electrode, a platinum helix down stream from the generating compartment as the auxiliary electrode, and a fiber type SCE as the reference electrode.

#### Electron Spin Resonance Spectra

Electron spin resonance spectra were measured on a Varian V4502 spectrometer with 100kc. modulation. The hyperfine coupling constants were measured by comparison with the known hyperfine coupling constant of a dilute, degassed benzene solution of di-t-butyl nitroxide which was placed in the second channel of the V4532 Dual sample cavity so that the standard and electrolytically produced radical could be run simultaneously. The decay of the radicals was followed by setting the magnetic field so that a maximum deflection was obtained from the radical spectrum and then, with the chart running, breaking the electrolytic circuit. The rate of chart travel is accurately known and hence the decay of the radical as a function of time was directly plotted by the recorder pen.

SECTION 11

STRUCTURAL CRITERIA FOR CHEMILUMINESCENCE COMPOUNDS

Certain key questions bearing on the chemiluminescence process can best be answered by the design and synthesis of new potentially chemiluminescent compounds having appropriately selected structural features. Three such objectives of prime importance have been described in the previous report<sup>2</sup>:

(A) Determination of essential structural characteristics required to provide an efficient mechanistic pathway for the conversion of chemical energy to electronic excitation energy.

(B) Determination of the effect of combining a highly fluorescent structure with a known chemiluminescent structure.

(C) Determination of the effect at high luminant concentration of incorporating a chemiluminescent structure into a polymeric backbone. The first objective deals with the basic mechanism of chemiluminescence. The second explores the possibility of increasing the efficiency of a known chemiluminescent reaction by increasing the fluorescent efficiency of the emitting species. The third objective attacks the general problem of efficiency loss at high luminant concentration.

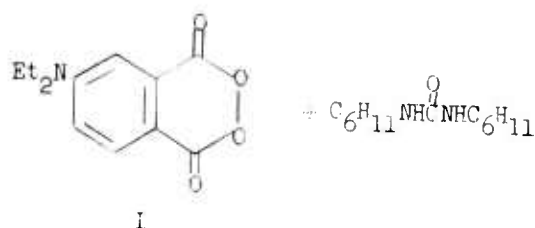
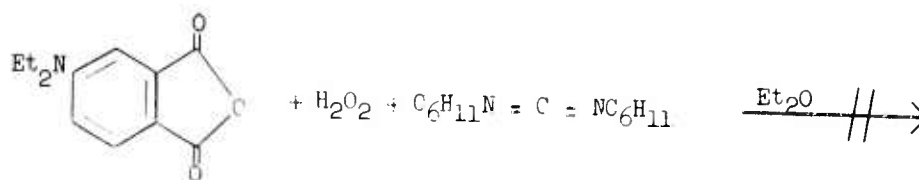
A. Formation of Electronically Excited Molecules

1. Relationship of peroxides to chemiluminescence

Attention has frequently been called to the fact that the known organic chemiluminescent reactions involve oxygen or hydrogen peroxide as a reactant. Indeed it has been shown that either oxygen or hydrogen peroxide is essential for appreciable chemiluminescence from 3-aminophthalhydrazide<sup>12</sup>. These observations imply that organic peroxides are intermediates in the known systems. Thus while a variety of oxidizing agents will oxidize 3-aminophthalhydrazide, only oxygen or hydrogen peroxide would be likely to provide a hydroperoxide intermediate and only the latter reactions are substantially chemiluminescent. A number of peroxidic compounds have been designed to test the generality of this implied relationship and to examine the relationship of structure to bright yield.

Synthesis of the acridine peroxides proposed in the previous report has been deferred to the third quarter. A number of unsuccessful attempts to prepare 4-diethylaminophthaloylperoxide, I, were also described in the last report.

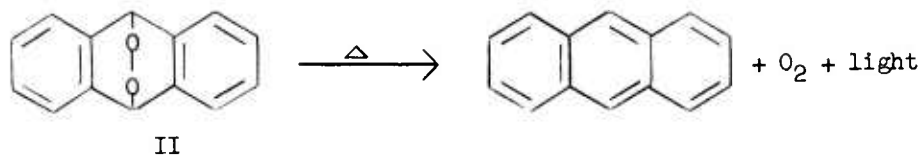
Recently a new, powerful but gentle, acyl peroxide synthesis has been reported involving reaction of a carboxylic acid with anhydrous hydrogen peroxide and a dialkylcarbodiimide<sup>4</sup>. The reaction was successfully applied to the preparation of phthaloyl peroxide<sup>4</sup>. Our attempts to use this procedure to prepare the peroxide, I, however, have failed.



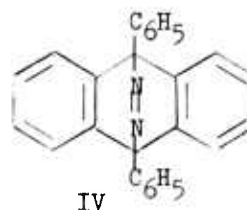
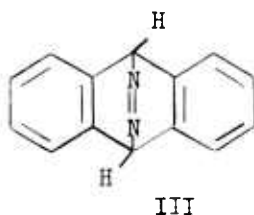
Evidently the amino group decreases the stability of the peroxide ring, and our efforts to prepare I will be terminated.

## 2. The Essential Requirement of Oxygen in Organic Chemiluminescence

While peroxides appear to be generally involved in organic chemiluminescent reactions, the question remains whether the elimination (or absorption) of oxygen is an essential process for light emission. On first consideration it would appear reasonable to achieve chemiluminescence using systems that in no way involve the oxygen molecule. Using the chemiluminescent decomposition of anthracene photoperoxide, II, as an example, one might expect the products to be ground state oxygen, which is known to involve two unpaired (triplet) electrons, and excited triplet anthracene. Triplet anthracene is required if electron spin is to be consumed in the reaction. Since decay of excited triplets has never produced luminescence in



oxygenated solution, this process would not be chemiluminescent. The chemiluminescence observed would then be ascribed to the formation of a small portion of excited singlet anthracene formed in violation of the spin conservation rule. Actually, violation of spin conservation might arise in such a system in view of the ability of oxygen to catalyze intersystem crossing. Nevertheless, according to this view one would expect greater chemiluminescence efficiency in an analogous system where intersystem crossing was not necessary to generate the anthracene singlet. An ideal system from this viewpoint would be 9,10-azo-9,10-dihydroanthracene, III, or the 9,10-diphenyl derivative IV.



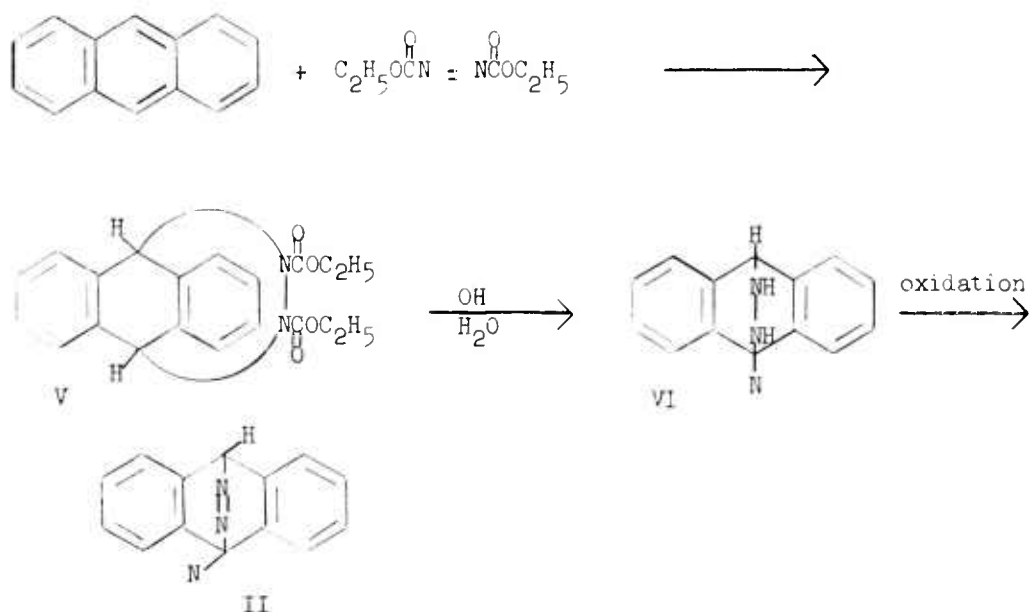
Elimination of ground state (singlet) nitrogen could leave the residual anthracene in a singlet state.

There is, however, an alternative viewpoint based on quantum mechanical considerations, which suggests that a triplet or

quasitriplet intermediate is necessary to produce excited molecules in preference to ground state molecules. This argument stems from the premise that singlet potential energy surfaces do not cross.

It is clearly necessary to resolve these opposing viewpoints experimentally. To attack this point directly, we are attempting to prepare azoanthracenes III and IV in order to compare their potential luminescence with the luminescence from the corresponding anthracene peroxides.

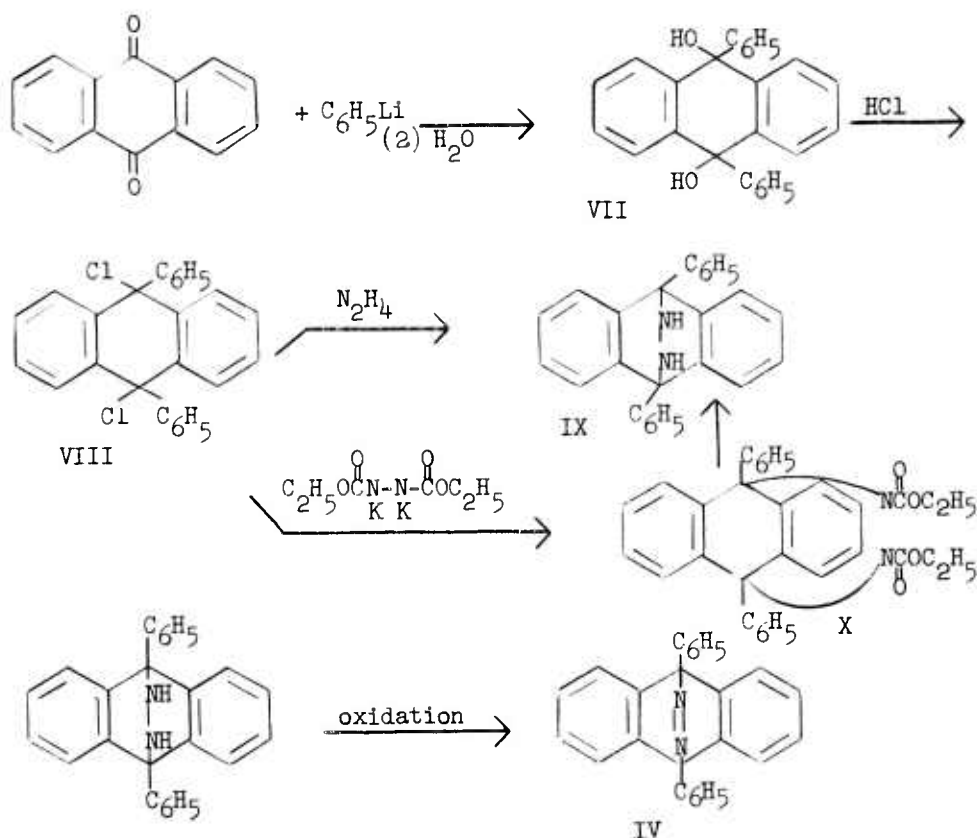
The preparation of 9,10-azoanthracene, II, is being attempted by the following route.





Addition of diethyl azodiformate to anthracene by a known procedure<sup>21</sup> proceeded satisfactorily to give the adduct V. Hydrolysis of V to the bridged hydrazo compound VI has recently been reported by Corey and Mock<sup>22</sup>. Our efforts to repeat their procedure, however, have failed thus far. Under relatively mild conditions unchanged V was recovered in high yield; under somewhat more vigorous conditions a variety of as yet unidentified products and anthracene have been isolated. Attempts will be made to achieve this hydrolysis under other conditions.

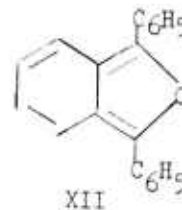
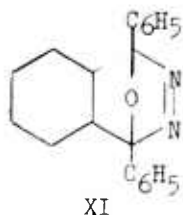
The preparation of III is being carried out by the following route.



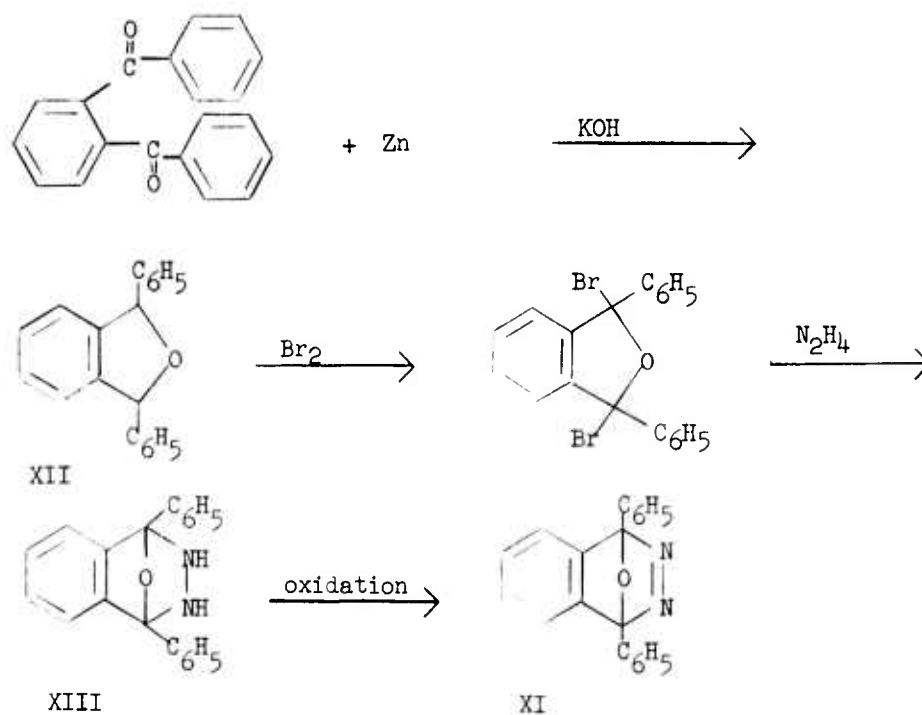
Reaction of anthraquinone with phenyllithium gave 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene, VII, and treatment of this with anhydrous hydrogen chloride gave the dichloroanthracene, VIII. Attempts will now be made to convert VIII to the bridged hydrazo anthracene IX by reaction with hydrazine or by reaction with dipotassium hydrazodiformate followed by hydrolysis.

An attempt was made to prepare adduct X directly from 9,10-diphenylanthracene and diethylazodiformate. Reaction did not occur, however, even after a prolonged reaction period.

Elimination of nitrogen from 1,4-diphenyl-1,4-epoxy-1,4-dihydrophthalazine, XI, might on the same basis, be expected to provide the highly fluorescent 1,3-diphenylisobenzofuran XII in an excited singlet state.



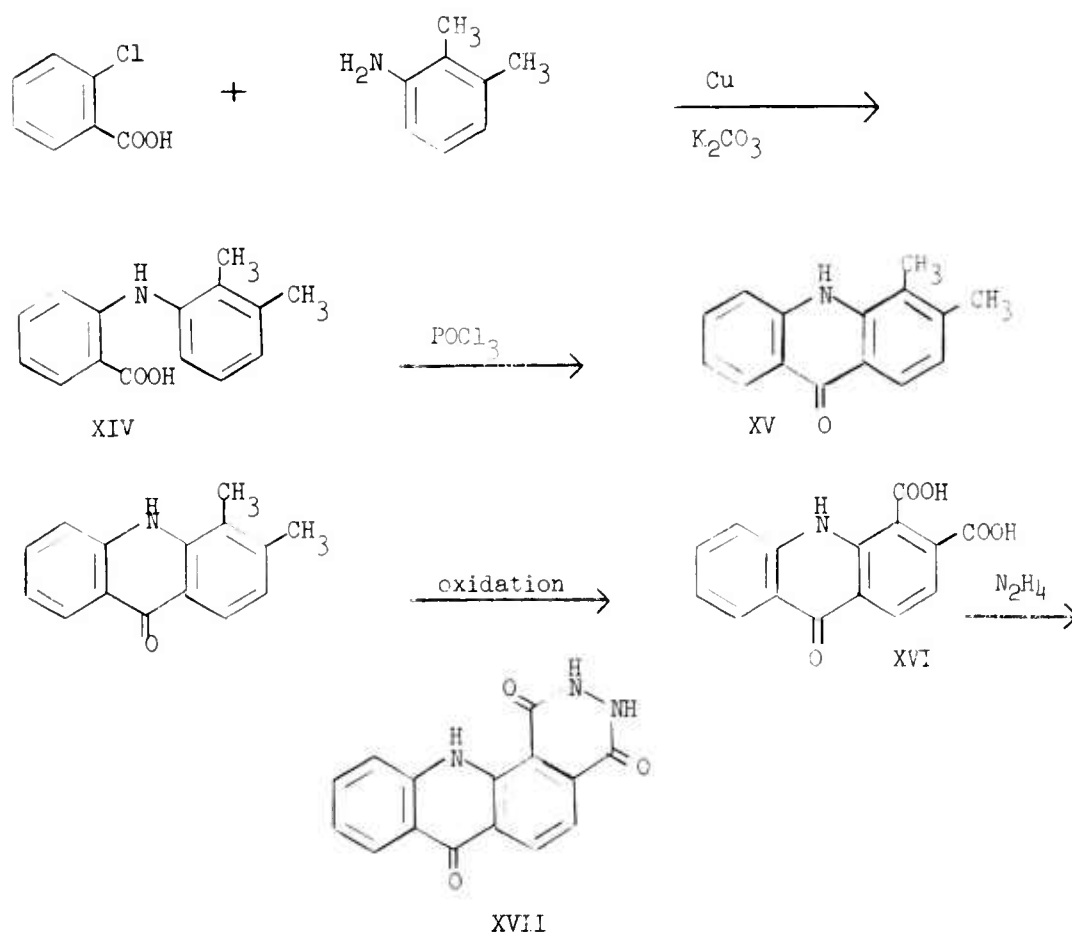
A brief attempt was made to prepare XI by the following route.



1,3-Diphenylisobenzofuran, XII, prepared by an established procedure<sup>23</sup> was reacted with bromine and the product was treated in situ with hydrazine to obtain a material analyzing poorly for the hydrazo compound, XIII. This material did not provide chemiluminescence on attempted oxidation.

B. Highly Fluorescent Phthalhydrazides

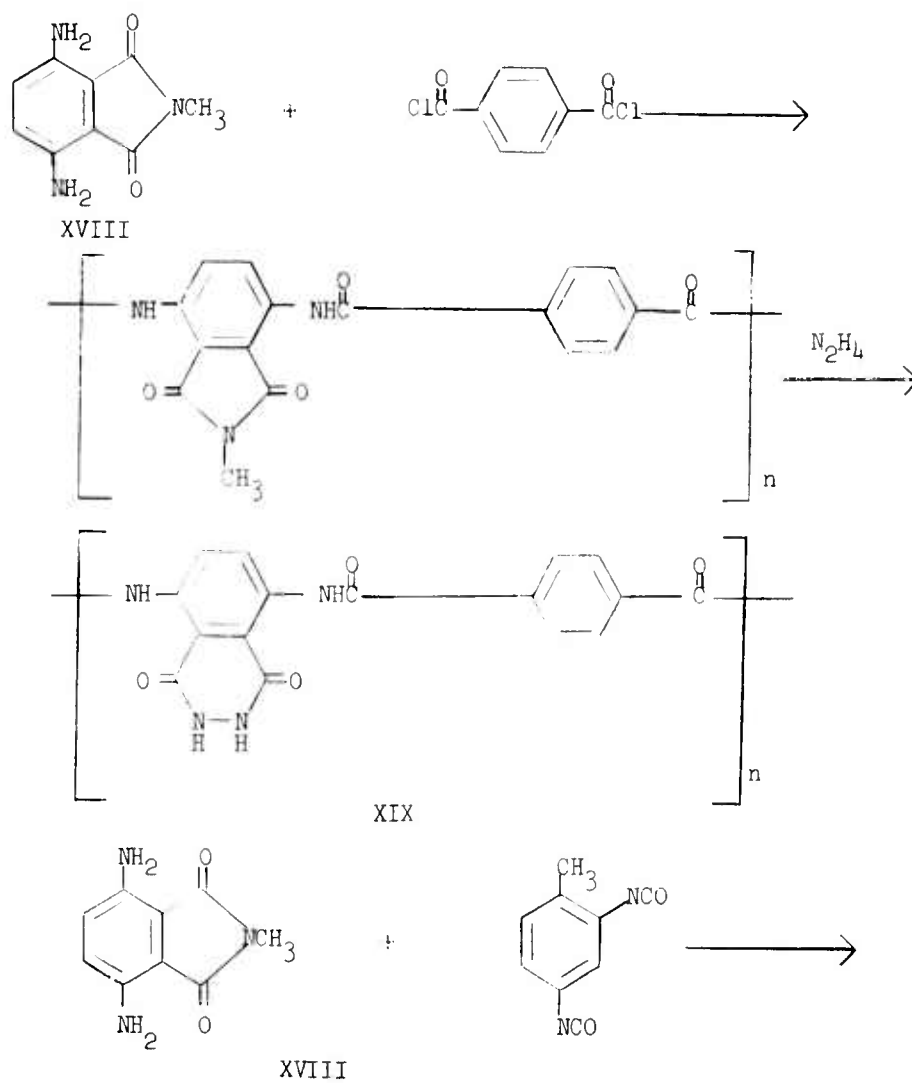
Efforts to prepare the phthalhydrazide acridone, XVII, described in the previous report<sup>2</sup>, have continued, with the following new synthetic route being investigated.

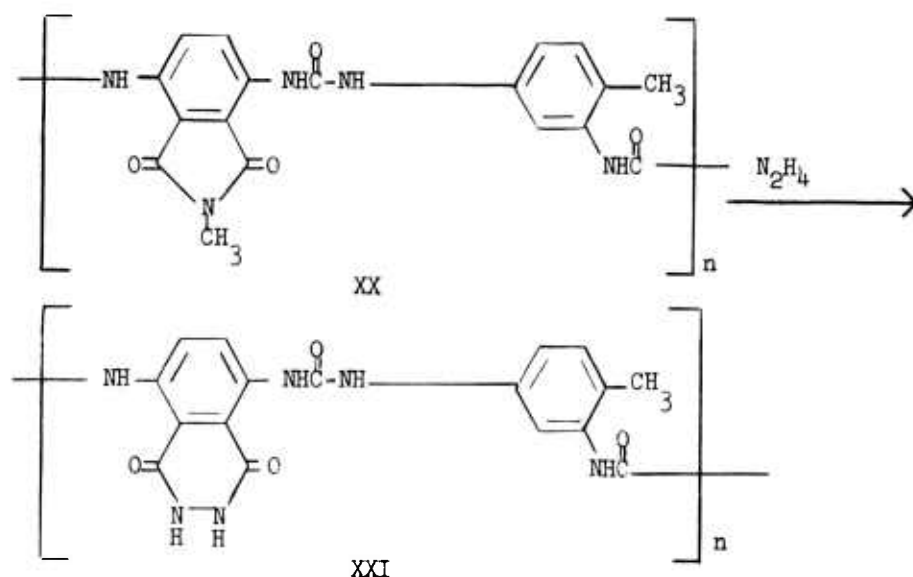


The Ullmann condensation of 2-chlorobenzoic acid with 2,3-dimethylaniline provided the diphenylamine, XIV, and ring closure with phosphorus oxychloride has given 3,4-dimethylacridone, XV. Initial attempts to oxidize XV with nitric acid, sodium dichromate, and sulfuric acid, or aqueous alkaline potassium permanganate, failed to give the dicarboxy acridone, XVI. However, oxidation with potassium permanganate in acetone has given a monocarboxylic acid product and it is likely that this can be further oxidized to XVI. Oxidation of XV to XVI with neutral sodium dichromate at 250° is also an attractive method which will be tried.

C. Polymeric Phthalhydrazides

As described in the previous report<sup>2</sup> we are attempting to prepare the polyamide XIX and the polyurea XXI by the routes indicated below.





Reaction of 3,6-diamino-N-methylphthalimide, XVIII, with terphthaloyl chloride by the interfacial polymerization method<sup>24</sup> has given a condensation product of very low molecular weight. Since the required high polymer was not obtained attempted synthesis of XIX will be discontinued.

Reaction of the diamine XVIII with 2,4-toluenediisocyanate in dimethylformamide solution<sup>24</sup> has given a product having the properties expected for the high molecular weight polyurea, XX. Attempts to convert the phthalimide structure to the required phthalhydrazide structure, XXI, are in process.

## SECTION II

### EXPERIMENTAL

#### Materials

4-Diethylaminophthalic anhydride and 3,6-diamino-N-methylphthalimide were prepared as described in the previous report<sup>2</sup>. 9,10-Dihydroxy-9,10-diphenyl-9,10-dihydroanthracene was prepared from anthraquinone and phenyl lithium<sup>25</sup>. Other starting materials were obtained from commercial sources.

#### 4-Diethylaminophthaloyl Peroxide

A solution of 1.00 g. (4.36 mmoles) of 4-diethylaminophthalic anhydride in 15 ml. methylene chloride was added to a solution of 0.94 g. (4.56 mmoles) dicyclohexylcarbodiimide in 15 ml. of 2.28 M anhydrous hydrogen peroxide in ether at 5°C. during 15 minutes. The reaction mixture was then maintained at 0-5° for 72 hours. Filtration of the reaction mixture gave 0.72 g. (72% of N,N'-dicyclohexyl urea, m.p. 231-233° (Lit.<sup>4</sup> m.p. 233-234°). The filtrate was washed three times with saturated ammonium sulfate solution, twice with 10% sodium carbonate solution, twice with saturated sodium chloride, then dried over anhydrous sodium sulfate. Concentration of the filtrate after drying gave 0.20 g. (20% of 4-diethylaminophthalic anhydride, identified by its infrared spectrum. No further products were found.

#### Diethylazodicarboxylate Adduct with Anthracene<sup>21</sup>

Diethylazodicarboxylate (37.4 g., 0.215 mole) was combined with a mixture of 38.0 g. (0.215 mole) of anthracene and 200 ml. of toluene. The reaction mixture was refluxed 24 hours, then allowed to stand at 0° for 20 hours. The white crystalline material was collected, washed with cold petroleum ether, and dried to obtain 38.1 g. (50.3%) of product, m.p. 136-7° (Lit.<sup>21</sup> m.p. 138°).

#### Attempted Hydrolysis of Diethylazodicarboxylate Adduct with Anthracene

A<sup>22</sup> 1. To 75 ml. of a stirred 2M solution of sodium ethoxide in ethanol freshly prepared from sodium metal and ethanol was added 38.1 g. (0.11 mole) of diethylazodicarboxylate adduct with anthracene. Water (2.7 g., 0.15 mole) was added to the mixture, which was then stirred 20 hrs. at 25° under nitrogen. One third of the solvent was evaporated at room temperature under reduced pressure, and the residue was poured into five volumes of cold water. The mixture was acidified with 10% hydrochloric acid and filtered to obtain 36.9 g. (97%) of unchanged starting material.



2. The experiment above was repeated at a reaction temperature of 40°. The acid insoluble material (88% recovery) was found to be starting material. The acidic filtrate from the recovered starting material was made alkaline with dilute aqueous sodium hydroxide to obtain a small amount of material, still containing a carbethoxy group according to infrared analysis, which appeared to be the mono hydrolysis product.

3. Using the above conditions, the hydrolysis reaction was carried out at room temperature using a twentyfold excess of 2N ethanolic sodium hydroxide. Two as yet unidentified products were obtained, but the desired product was not found.

A total of six reactions were carried out under similar conditions, varying the reaction time from 16 hrs. to 40 hrs., the reaction temperature from 25° to 40°, and the base strength from a 25% excess to 2000% excess. Under the more vigorous sets of conditions the products recovered were anthracene and the apparent "half-hydrolysis" product. Under milder conditions the starting material was recovered.

B. To a solution of 11.0 g. (0.2 mole) of potassium hydroxide in 8 ml. water and 31 ml. of methanol (Claisen's alkali) was added 5.0 g. (0.014 mole) of diethylazodicarboxylate adduct with anthracene. The reaction mixture was stirred 20 hrs. at 25°, then added to 10 volumes of water. The mixture was acidified with 10% hydrochloric acid, filtered, and made basic with 5% sodium hydroxide. All operations were carried out at room temperature. Basic products were not found. Unchanged starting material (3.9 g., 78%) was recovered as the acid insoluble product.

A total of three Claisen's alkali hydrolyses were attempted with reaction times ranging from 20 hrs. to 5 min., and reaction temperatures ranging from 25° to reflux. No product was obtained.

Table 1

Summary of Claisen's Alkali Hydrolyses Attempts

<u>Weight Starting Material</u>	<u>Base Strength</u>	<u>Reaction Time</u>	<u>Reaction Temperature</u>	<u>Per Cent S.M. Recovered</u>	<u>Per Cent Products Obtained</u>
5.0 g.	5.0M	20 hrs.	25°	78	-
5.0 g.	5.0M	4 hrs.	40°	70	-
5.0 g.	5.0M	5 min.	Reflux	72	-

Attempted Preparation of the Diethylazodicarboxylate Adduct with 9,10-Diphenylanthracene

A solution of 5.0 g. (0.015 mole) of 9,10-diphenylanthracene and 2.6 g. (0.015 mole) of diethylazodicarboxylate in 50 ml. of toluene was refluxed for 7 days under a 150 watt incandescent light bulb. The solution was cooled, and the yellow precipitate was collected, washed with cold toluene, and dried to obtain 4.2 g. (84%) of unchanged 9,10-diphenylanthracene.

9,10-Dichloro-9,10-diphenyl-9,10-dihydroanthracene<sup>26</sup>

A continuous stream of anhydrous hydrogen chloride was passed over a vigorously stirred solution of 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene (6.0 g., 0.016 mole) in 45 ml. of chloroform for a period of 25 min. The reaction mixture was protected from moisture with a drying tube, and stirred 16 hrs. at 25°.

Glacial acetic acid (90 ml.) was added with stirring to the reaction mixture, and the precipitate was collected, washed with cold benzene, and dried to obtain 5.1 g. (79.7%) of material, m.p. 196-7° (Lit.<sup>26</sup> m.p. 202°).

Anal. Calcd. for  $C_{12}C_2H_{18}$ : C, 77.81; H, 4.52; Cl, 17.67.

Found: C, 77.60; H, 4.81; Cl, 17.73.

A similar experiment, employing a 1 hr. reaction time, gave a product, m.p. 210-12° (dec.), that appeared from infrared and elemental analyses to be 9,10-diphenyl-9-chloro-10-hydroxy-9,10-dihydroanthracene.

Anal. Calcd. for  $C_{11}C_2H_{19}O$ : C, 81.55; H, 5.00; O, 4.18; Cl, 9.26.

Found: C, 80.96; H, 4.91; O, 4.50; Cl, 9.79.

1,3-Diphenylisobenzofuran<sup>23</sup>

A mixture of 5.4 g. (0.018 mole) o-dibenzoylbenzene, 5.4 g. sodium hydroxide and 200 ml. of 95% ethanol were refluxed with vigorous stirring in a Morton flask until a clear red-brown solution was obtained. Powdered zinc (5.3 g.) was added and refluxing was continued until the liquid portion of the mixture became yellow. About eight minutes was required. The hot mixture was filtered and the resulting filtrate was poured into 25 ml. conc. hydrochloric acid. A bright yellow precipitate separated and was collected. Recrystallization from petroleum ether gave 2.1 g. (54%) of bright yellow needles, m.p. 125-126° (Lit.<sup>23</sup> 125-126°).

The use of a Morton flask and careful control of the reaction time was required to obtain satisfactory results.

Attempted Preparation of 1,2,3,4-Tetrahydro-1,4-diphenyl-1,4-epoxyphthalazine

A solution of 0.77 g. (0.096 mole) bromine in 10 ml. chloroform was added dropwise to a stirred solution of 1.3 g. (0.048 mole) of 1,3-diphenylisobenzofuran in 25 ml. of chloroform at 3-5°. The reaction mixture was refluxed for two hours. A 150 watt light was then placed next to the flask, and reflux was continued for an additional 3 hrs. At the end of this period the condensate was colorless. To this mixture were added 0.271 g. of 64% aqueous hydrazine solution and 0.80 g. of solid sodium bicarbonate. A slight exotherm resulted and the color changed from red to brown. After remaining at room temperature for two days the solution was warmed and filtered. The filtrate was dried over sodium sulfate and evaporated to dryness. The residual dark orange solid was extracted with petroleum ether (b.p. 30-60°), leaving 0.835 g. of insoluble brown crystals. This material was recrystallized from a benzene hexane mixture to give light tan crystals, m.p. 194-196°.

Anal. Calcd. for  $C_{20}H_{16}NO_2$ : C, 80.00; H, 5.37; N, 9.33.

Found: C, 85.39; H, 5.17; N, 9.07.

2,3-Dimethyl-2'-carboxydiphenylamine

A mixture of 90 g. (0.57 mole) of o-chlorobenzoic acid, 109 g. (0.79 mole) of anhydrous potassium carbonate and 228 g. (1.88 moles) of 2,3-dimethylaniline was refluxed for 30 min. The water formed was removed by azeotropic distillation. The solution was cooled slightly and 2 g. of activated copper<sup>27</sup> and 0.5 g. each of cupric oxide, cupric acetate and cuprous chloride were added. The solution was refluxed for 5 hrs. at 173°. The excess aniline was removed by steam distillation and the non-volatile residue was treated with acetic acid to obtain 48 g. (35%) of brown crystals. Recrystallization from ethanol gave 27.4 g. (20%) of material, m.p. 226-228° dec.

Anal. Calcd. for  $C_{15}H_{15}NO_2$ : C, 74.51; H, 6.06; N, 6.14.

Found: C, 74.68; H, 6.27; N, 5.31.

Three attempts to obtain this product via the standard Ullmann condensation in amyl alcohol solution<sup>28</sup> gave yields of only 5-8%.

### 3,4-Dimethylacridone

2,3-Dimethyl-2'-carboxydiphenylamine (28.35 g., 0.11 mole) was combined with 200 ml. of phosphorous oxychloride and the mixture was refluxed for 2.5 hrs. The excess phosphorous oxychloride was removed by distillation under reduced pressure. The residue was treated with 300 ml. of 1N hydrochloric acid, and the resulting solution was heated at reflux for two hours. The solid which separated during reflux was collected and recrystallized from ethanol to obtain 7.85 g. (32%) of yellow crystals, m.p.  $> 340^\circ$ . The infrared spectrum of the product was in good agreement with that expected for the desired product. Analytical results are pending.

### 3,4-Dicarboxyacridone

A. Nitric acid - A mixture of 1.0 g. of 3,4-dimethylacridone, 10 ml. of 70% nitric acid and 20 ml. water was refluxed for 30 hours. The reaction mixture was poured over ice and the resulting mixture was filtered to obtain a dark yellow solid, melting above  $310^\circ$ . The infrared spectrum indicated that the product was a nitroacridone rather than the desired product.

B. Sodium dichromate - To a solution of 2.1 g. of 3,4-dimethylacridone in 100 ml. of conc. sulfuric acid was added 6.2 g. of sodium dichromate during two hours at  $25-30^\circ$ . The temperature was then raised to  $45-55^\circ$  for two hours and the mixture was cooled and poured over ice. After standing overnight a small amount of solid was obtained. This was dissolved in 5% sodium bicarbonate, treated with activated charcoal and reprecipitated with hydrochloric acid. The infrared spectrum indicated that the solid was unchanged starting acridone.

C. Potassium permanganate - A mixture of 0.2 g. (0.001 mole) of 3,4-dimethylacridone and 0.316 g. of potassium permanganate in 25 ml. of acetone was stirred at room temperature for two days. The excess potassium permanganate was destroyed with ethanol, sodium bicarbonate was added to make the solution basic and the mixture was filtered. The filtrate was reduced to 15 ml. under reduced pressure, acidified with hydrochloric acid and filtered. The solid was washed with water and dried. The infrared spectrum indicated that only one of the two methyl groups had been oxidized, and that the solid was a methyl carboxy acridone.

The solid (ca. 0.1 g.) was dissolved in 5 ml. of 1.6N sodium hydroxide, and treated with 0.15 g. of potassium permanganate. The solution was refluxed for three hours. The excess potassium permanganate was destroyed with ethanol, and the mixture was filtered.

Acidification of the filtrate with hydrochloric acid gave a small amount of precipitate, m.p.  $>300^{\circ}$ , having an infrared spectrum in agreement with that expected for the desired dicarboxyacridone.

Other attempts to oxidize the dimethyl acridone with excess potassium permanganate at reflux in either water or 1.6 N sodium hydroxide gave only unchanged starting material.

Attempted Preparation of a Polyamide from 3,6-diamino-N-methylphthalimide and Sebacyl Chloride

To a vigorously stirred solution of 1.8 g. (0.01 mole) of 3,6-diamino-N-methylphthalimide and 2.2 g. (0.02 mole) of sodium carbonate in 100 ml. of water was added over a period of 10 seconds a solution of 2 ml. of sebacyl chloride in 100 ml. of 1,1,1-trichloroethane. The reaction mixture was stirred 24 hrs. at room temperature. The yellow-brown insoluble product was collected and washed twice with 10% hydrochloric acid. The acid insoluble material was filtered, washed with water, and dried over phosphorous pentoxide under vacuum for 8 hrs.

The properties and infrared spectrum of the material indicated a low molecular weight. This was confirmed by a molecular weight determination (freezing point depression in dimethylsulfoxide) which gave a value of 224.5%.

Preparation of a Polyurea from 3,6-Diamino-N-methylphthalimide and Toluene, 2,4-Diisocyanate

3,6-Diamino-N-methylphthalimide (4.7808 g., 0.025 mole) was dissolved in 25 ml. dry dimethylformamide. To the stirred solution was added in one portion a solution of 4.3549 g. (0.025 mole) of freshly redistilled toluene, 2,4-diisocyanate in 25 ml. dry dimethylformamide. The reaction mixture was protected from moisture, and stirred 18 hrs. at room temperature. The reaction mixture was poured with vigorous stirring into 400 ml. of water, and the resulting mixture was centrifuged. The resulting solid was washed with acetone and dried to obtain 2.0 g. (24.6%) of material. The infrared spectrum was in good agreement with that expected for the desired polymer. Elemental and molecular weight analyses are pending.

The centrifugate was combined with an equal volume of acetone and digested on the steam bath for 1 hr. The solvents were evaporated under reduced pressure and the gelatinous residue was dried over potassium hydroxide under vacuum for 60 hrs. to obtain approx. 5 g. (61.5%) of material, whose infrared spectrum was identical to that of the first product of the reaction.

### SECTION III

#### SPECTROSCOPY AND ENERGY TRANSFER

Final calibration of the Spectroradiometer-Fluorimeter<sup>2</sup> was completed after making some minor changes in the calibration and operational techniques. Further experiments will be performed at various time intervals to check the calibration. A 1P21 photomultiplier tube was substituted for the 1P22 tube to improve sensitivity. Its calibration was performed by reference to the 1P22 tube already calibrated by the technique described in the previous report<sup>2</sup>.

Computer programs were written to convert observed intensity values to absolute intensity units in terms of the calibration factors. The computer print-out gives the intensity at 50 angstrom intervals and the total intensity, which is obtained by integration over the spectral region. An absolute emission curve can then be traced to graphically illustrate the spectral distribution of any light source. The computer was also programmed to convert the absorbance of a sample (obtained on a Cary Model 16 Spectrophotometer) to the absolute quantity of light absorbed from the BLB illuminating lamps<sup>2</sup>. This result is also printed out in quanta/sec. and microwatts and is used to calculate the fluorescence quantum yield of a sample.

A Leeds and Northrup Disc integrating recorder has also been attached to the amplifier to obtain intensity vs. time integrations directly for emissions that do not decay exponentially.

Emission spectra and quantum yields of various fluorescent compounds were determined using several concentrations to study the effects of concentration quenching. Fluorescence quantum yields are summarized in Table I. Comparisons with literature values are provided in Table II. The more dilute samples (with a minimum of quenching) compared very favorably with the literature values. Fluorescence quantum yields were also obtained on the yellow fluorescent dyes as described in the last report and are listed in Table III.

The reaction of 3-aminophthalhydrazide with aqueous potassium persulfate and hydrogen peroxide was investigated, with the reaction rate, the spectral distribution and the absolute quantum yield being determined. The second order rate constant at 29° was found to be  $1.4 \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$  and did not change substantially in the presence of ethylenediaminetetraacetic acid (see Section I, p. 14). The rate constant at 35.9° was  $1.6 \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ . A typical spectral curve is shown in Figure 3. The chemiluminescent quantum yield under these conditions closely approaches 1%. Rate and quantum yield data are summarized in Table IV.

Addition of  $4 \times 10^{-4}$  molar disodium fluorescein to the aqueous 3-aminophthalhydrazide reaction has little effect on the quantum yield although 82% of the emission under these conditions is characteristic of fluorescein. (See Figure 4.) Resonance energy transfer, which might be expected to increase the quantum yield, is apparently absent from this system. Additional experiments will be carried out at high

fluorescein concentration when energy transfer is more probable.

The quantum yield and spectral distribution of chemiluminescence from the reaction of oxalyl chloride with anhydrous hydrogen peroxide and 9,10-diphenylanthracene in ether were successfully determined although the decay rate was very rapid under the conditions employed. The quantum yield was found to be on the order of 6%, making this reaction one of the most efficient known. However, the quantum yield was measured under conditions where the oxalyl chloride concentration was very low and there is evidence that the yield decreases with increasing concentration. Nevertheless, a study of reaction conditions, now in progress, may well increase the efficiency further. The spectral distribution of the emission was measured photographically with a Hilger medium quartz spectrograph and is pictured in Figure 5. A comparison of the chemiluminescence spectrum with the normal fluorescence spectrum of 9,10-diphenylanthracene is also provided in the figure. While the spectra are quite similar the differences are believed to be significant and will be examined further. An attempt will be made to study the kinetics, quantum yields, and concentration effects at low temperature.



Table I

Fluorescence Data

<u>Fluorescent Compound</u>	<u>Concentration</u> <u>Moles per Liter x 10<sup>5</sup></u>	<u>Quantum Yield-Measured</u>
Fluorescein in 0.1 <u>N</u> NaOH	700	0.25
"	130	0.72
"	50	0.86
"	5	0.92
Rhodamine B in Ethanol	240	0.41
"	48	0.45
"	19	0.49
"	0.38	0.99
Anthracene in Ethanol	600	0.21
"	47	0.29
"	9	0.30
"	1.8	0.50
Eosin in 0.1 <u>N</u> NaOH	400	0.03
"	120	0.08
"	40	0.14
"	18	0.17

Table II

Comparison of Fluorescence Quantum Yield Values  
with Values from the Literature

<u>Compound</u>	<u>Solvent</u>	<u>Quantum Yields and (References)</u>	<u>Result from Table I*</u>
Disodium Fluorescein	0.1 <u>N</u> NaOH	0.85 <sup>(29)</sup> , 0.93 <sup>(30)</sup> , 0.79 <sup>(31)</sup> , 0.80 <sup>(32)</sup> , 0.85 <sup>(33,34)</sup> , 93 <sup>(35)</sup> , 72 <sup>(36)</sup>	0.92
Rhodamine B	Ethanol	0.69 <sup>(29)</sup> , 0.97 <sup>(30)</sup> , 0.93 <sup>(34)</sup>	0.99
Anthracene	Ethanol	0.28 <sup>(29)</sup> , 0.26 <sup>(33)</sup> , 0.30 <sup>(35)</sup>	0.50
Disodium Eosin	0.1 <u>N</u> NaOH	0.23 <sup>(29)</sup> , 0.19 <sup>(30)</sup> , 0.12 <sup>(31)</sup> , 0.15 <sup>(32)</sup> , 0.20 <sup>(35)</sup>	0.17

\* Values in Table I for the most dilute solution.

Table III

Quantum Yields of Fluorescent Dyes

Compound	Concentration	Quantum Yield
Calcofluor Yellow H.E.B. super conc.	0.01 gm/100 ml in Methanol	0.77
Calcofluor Yellow 7B	0.01 gm/100 ml in Methanol	0.50
Calcofluor Yellow 6G	0.01 gm/100 ml in Methanol	0.41
Calcofluor White 5B conc.	0.01 gm/100 ml in Methanol	0.86

Table IV

Rate Constants and Absolute Quantum Yields for the  
3-Aminophthalhydrazide- $K_2S_2O_8$ - $H_2O_2$  Reaction in Sodium Carbonate<sup>(a)</sup>

Exp.	Additive	Temperature (degrees, C)	k l. mole <sup>-1</sup> sec <sup>-1</sup>	Normalized Spectral Area	Q.Y. %
1	None	29.0	$1.4 \times 10^{-2}$	20.3	0.95
2	None	35.9	$1.6 \times 10^{-2}$	19.8	0.94
3	EDTA <sup>(b)</sup> ( $1 \times 10^{-4}$ molar)	29.0	$1.2 \times 10^{-2}$	20.3	0.97
4	Disodium fluorescein ( $4 \times 10^{-4}$ molar)	29.0	-	12.1 <sup>(c)</sup> 10.2 <sup>(d)</sup>	1.02 <sup>(e)</sup>

(a) Concentrations for all experiments were: 3-aminophthalhydrazide =  $4 \times 10^{-3}$  molar,  $K_2S_2O_8$  =  $6 \times 10^{-2}$  molar,  $H_2O_2$  =  $3 \times 10^{-2}$  molar,  $Na_2CO_3$  = 0.1 molar.

(b) Ethylenediaminetetraacetic acid.

(c) Fluorescein band.

(d) 3-Aminophthalhydrazide band.

(e) Eighty-two percent of the emission was from the fluorescein band.

FIGURE 1  
FLUORESCENCE SPECTRUM OF FLUORESCIN IN 0.1 M AQUEOUS  $\text{Na}_2\text{CO}_3$

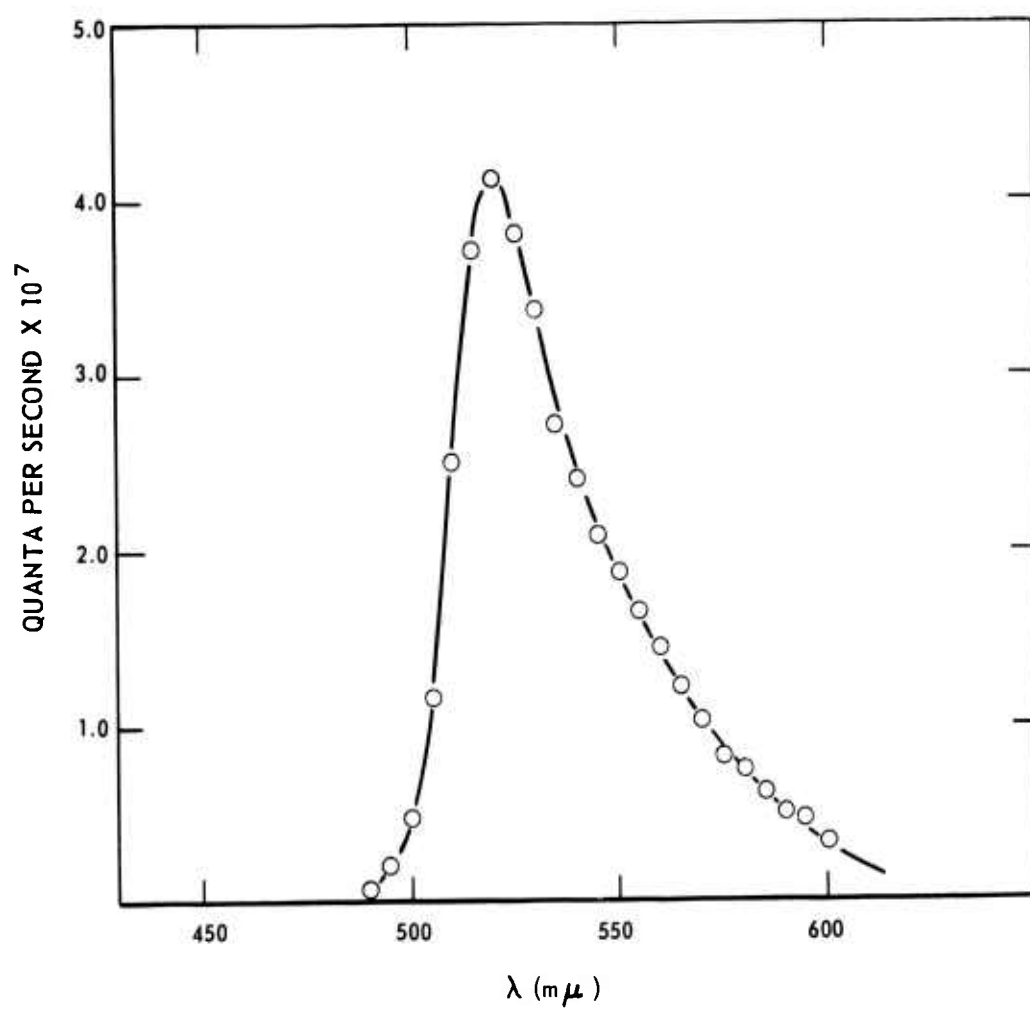


FIGURE 2  
LUMINESCENCE DECAY OF THE 3-AMINOPHTHALHYDRAZIDE  
 $K_2S_2O_8 - H_2O_2 - Na_2CO_3$  REACTION AT 29.0°C.

A: STANDARD RUN

B: EDTA ADDED

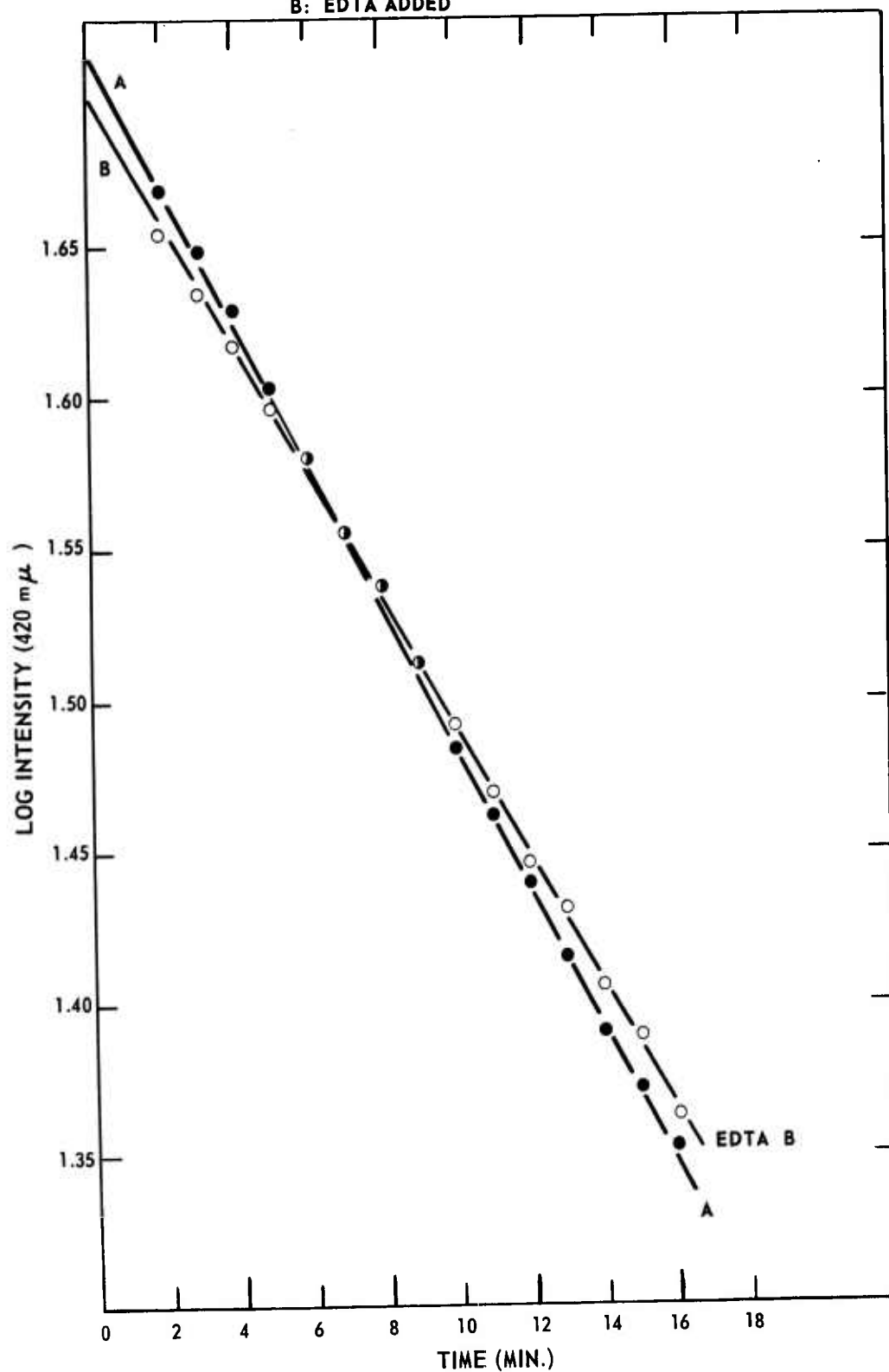


FIGURE 3  
SPECTRAL DISTRIBUTION OF THE 3-AMINOPHTHALHYDRAZIDE-  
 $K_2S_2O_8-H_2O_2$  REACTION IN 0.1 M  $Na_2CO_3$

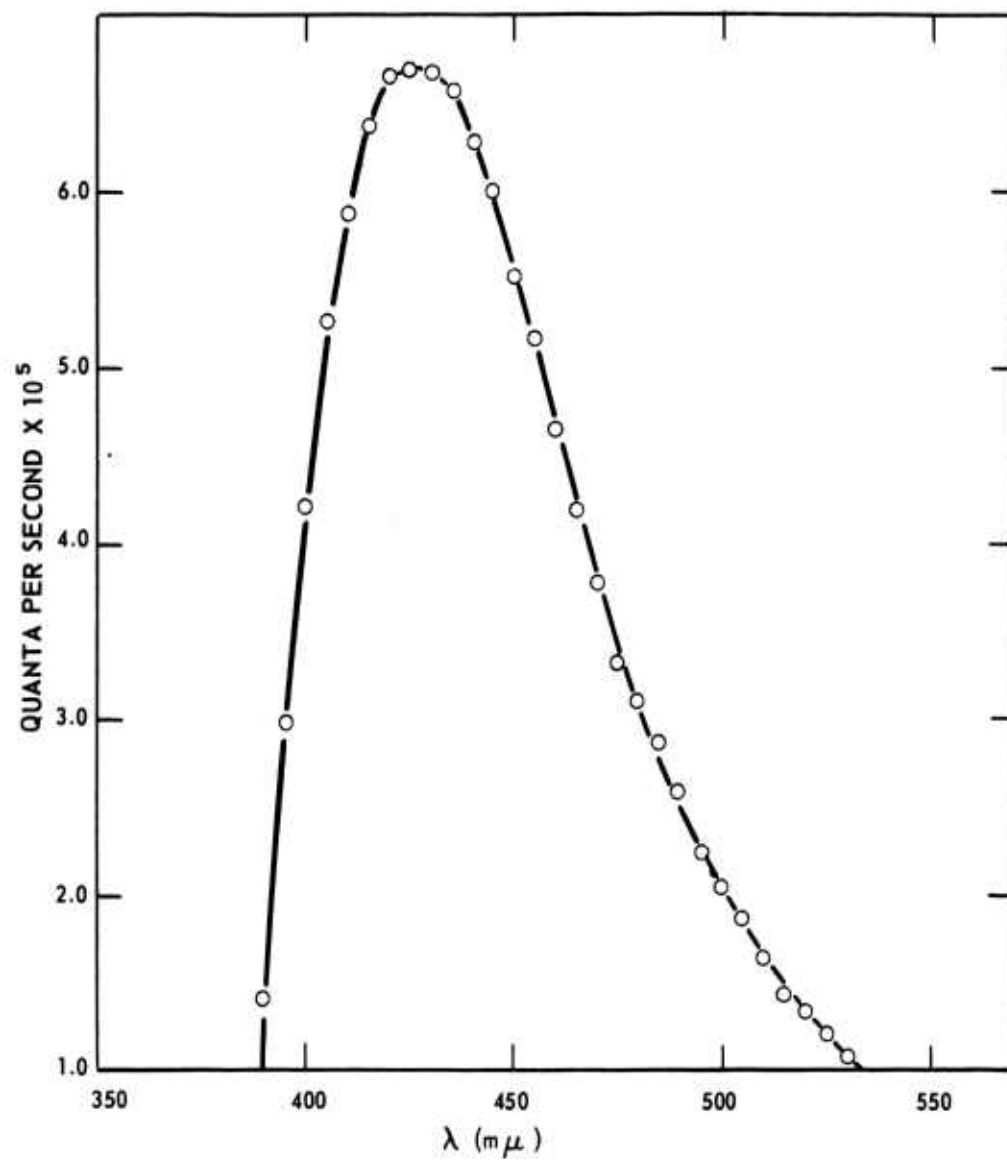


FIGURE 4  
EFFECT OF FLUORESCCEIN ( $4 \times 10^{-4}$  MOLAR) ON 3-AMINOPHTHALHYDRAZIDE  
CHEMILUMINESCENCE IN  $0.1 \text{ M}$  AQUEOUS  $\text{Na}_2\text{CO}_3$

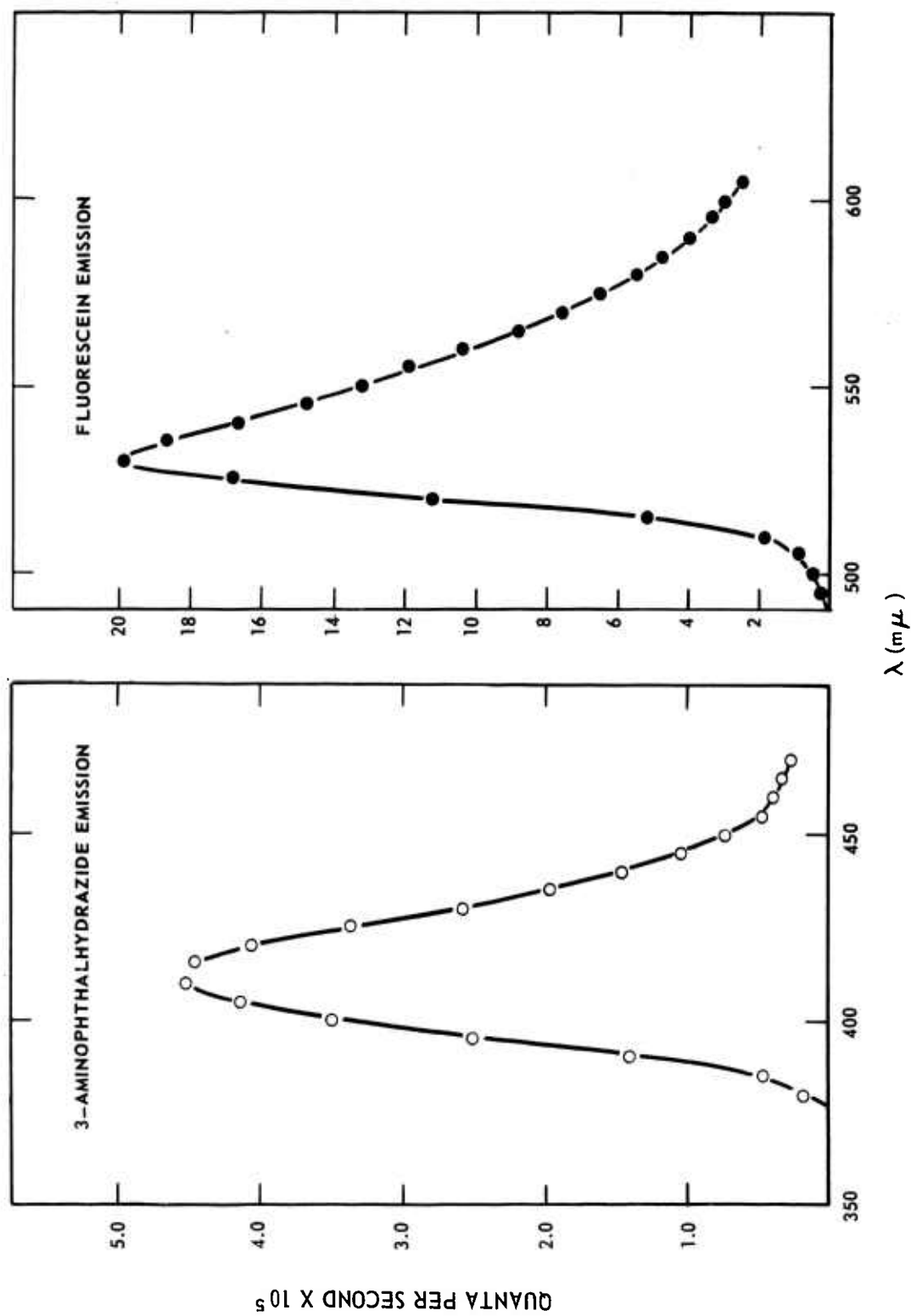
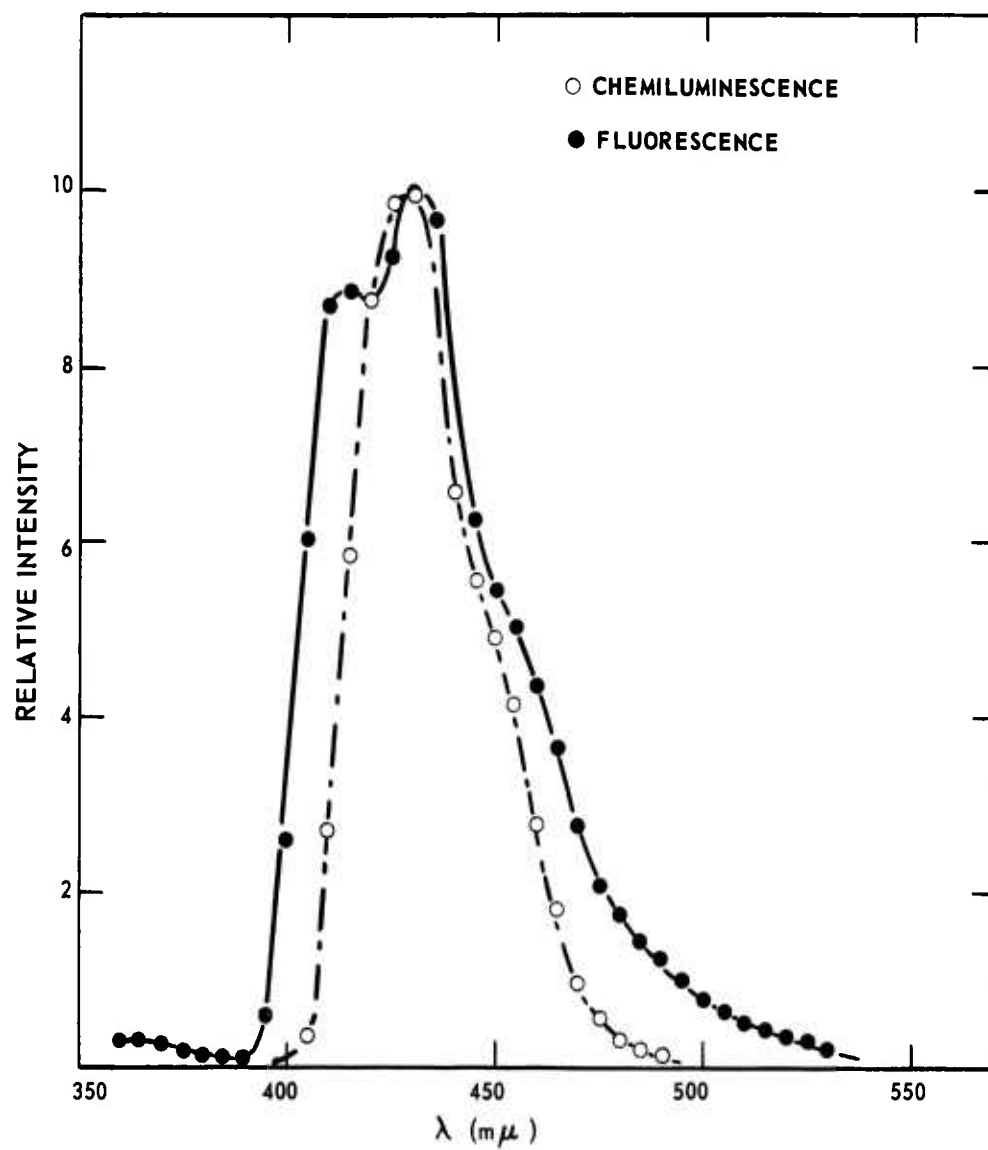


FIGURE 5  
SPECTRAL DISTRIBUTION OF THE OXALYL CHLORIDE-HYDROGEN PEROXIDE  
9,10-DIPHENYLANTHRACENE REACTION





SECTION III

EXPERIMENTAL

Fluorescence Quantum Yield Measurements

Fluorescence quantum yields are calculated on the basis of the following equation:

$$Q.Y = \frac{\text{absolute total intensity (quanta/sec.)}}{\text{total light absorbed (quanta/sec.)}}$$

The numerator value was obtained by measuring the spectral distribution from a solution sample with the instrument described in the previous report<sup>2</sup>. Measurements were made at 5 mμ intervals, and the observed intensity value at each wavelength was corrected by the calibration factor for that wavelength by a computer, programmed with the calibration data. The absolute intensity values were then integrated with respect to wavelength by the computer to obtain the total intensity in absolute quanta.

The absorption spectrum of the sample was measured using a Cary Model 14 spectrophotometer. A programmed computer then multiplied the fraction of light absorbed at each wavelength by the absolute intensity of exciting light reaching the sample at that wavelength as determined during the calibration. The computer then integrated the light absorbed at each wavelength over the spectral range to obtain an absolute value for the total light absorbed. Typical fluorescence spectra are pictured in Figures 1 and 5, and fluorescence quantum yield values are summarized in Table I.

Reaction Kinetics and Quantum Yield of the 3-Aminophthalhydrazide-K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>-H<sub>2</sub>O<sub>2</sub>-Na<sub>2</sub>CO<sub>3</sub> Reaction

This experiment, a repeat of one of a series of earlier experiments, was carried out on an absolute intensity basis. It had been established previously that under the pseudo first order reaction conditions employed the intensity was an accurate monitor of the 3-aminophthalhydrazide concentration<sup>12</sup>. This permits the reaction rate to be followed by measurement of light intensity. Thus the first order integrated rate equation (1) can be used in the form of equation (2)<sup>37</sup>.

$$(1) \ln \frac{I_0}{I} = k' T$$

$$(2) \ln \frac{I_0}{I} = k' T$$

where  $L_0$  is the initial concentration of 3-aminophthalhydrazide,  $L$  is the concentration at time  $T$ ,  $I_0$  is the initial emission intensity,  $I$  is the intensity at time  $T$ , and  $k'$  is the pseudo first order rate constant. Since the reaction was previously found to be first order in 3-aminophthalhydrazide, first order in  $K_2S_2O_8$ , zero order in the  $H_2O_2$ , and zero order in base, the second order rate constant  $k$  is calculated according to equation (3), and the actual rate expression is equation (4).

$$(3) \quad k = \frac{k'}{[K_2S_2O_8]}$$

$$(4) \quad \frac{dI}{dT} = \frac{dL}{dT} = k [L] [K_2S_2O_8]$$

The stock solutions ( $2 \times 10^{-2}$  molar 3-aminophthalhydrazide,  $2 \times 10^{-1}$  molar  $K_2S_2O_8$ ,  $6 \times 10^{-1}$  molar  $H_2O_2$ , and 2 molar sodium carbonate) were thermostated in a constant temperature bath at the desired temperature, and appropriate aliquots were mixed in a small thermostated flask. The persulfate solution was always added last, and the timer was started with this addition. An aliquot of the reaction mixture was quickly transferred to the thermostated quartz cell of the instrument and the intensity at 420 mμ was measured as a function of time. Plots of  $\log I_0$  vs. time were linear as indicated in Figure 2. Results of several experiments are summarized in Table 4.

Calculation of quantum yields requires measurement of the spectral distribution of the emission as well as intensity-time data. Previous experiments have demonstrated that the shape of the spectral curve is independent of reaction time. The spectral measurements required less than two minutes; only a negligible error was introduced by the reaction decay during this short interval.

The equation used to calculate the total quanta emitted was derived from the general equation (5).

$$(5) \quad Q = \int_0^{\infty} \int_{\lambda_1}^{\lambda_2} I_{\lambda} dT d\lambda$$

In this equation  $Q$  is the total quanta emitted,  $I_{\lambda}$  is intensity at wavelength  $\lambda$  in absolute units, which is obtained by applying the necessary correction factors from the calibration to the observed intensity values,  $T$  is time and  $\lambda$  is wavelength. Since the spectral distribution is not a function of time the double integral (5) is

equivalent to the simpler equation (6).

$$(6) \quad Q = \left( \int_0^{\infty} I_{\lambda_{ob}} dT \right) \left( \frac{\int_{\lambda_1}^{\lambda_2} I_{\lambda}^T d\lambda}{I_{\lambda_{ob}}^T} \right)$$

The first product term in (6) corresponds to the area under the intensity time curve measured at  $\lambda_{ob}$ . Since  $\log I_{\lambda_{ob}}$  plots vs. time were linear this integral was calculated from equation (7).

$$(7) \quad \text{decay area} = \int_0^{\infty} I_{\lambda_{ob}} dT = \frac{I_{\lambda_{ob}}^0}{k'}$$

$I_{\lambda_{ob}}^0$  is the initial intensity;  $k'$  is the pseudo first order rate constant.

The second product term in (6) corresponds to the spectral area per unit intensity at  $\lambda_{ob}$  measured at time T. This can be determined geometrically from the area of a plot of

$$\frac{I_{\lambda}^T}{I_{\lambda_{ob}}^T} \quad \text{vs.} \quad \lambda \quad \text{but is more conveniently calculated by}$$

an appropriately programed computer. Some typical spectral distributions are pictured in Figures 3, 4 and 5. The final equation for the quantum yield calculations then becomes:

$$Q.Y. = \frac{I_{\lambda_{ob}}^0}{k' \left[ \text{molecules of 3-aminophthalhydrazide} \right]} \frac{\int_{\lambda_1}^{\lambda_2} I_{\lambda}^T d\lambda}{I_{\lambda_{ob}}^T}$$

absolute quantum yield results from various experiments are summarized in Table 4.

Quantum Yield of the Oxalyl Chloride-Anhydrous Hydrogen Peroxide- 9,10-diphenylanthracene Reaction

Into the standard 3-ml. quartz light measurement cell was placed 1.7 ml. of 0.01 molar 9,10-diphenylanthracene in ether, and 1.0 ml. of 1.0 molar anhydrous ethereal hydrogen peroxide. The photomultiplier shutter was opened, the monochromator was adjusted to measure a wavelength of 430 mμ, the recorder was started, and 0.020 ml. of 0.75 molar ethereal oxalyl chloride was rapidly injected into the cell. The intensity vs. time relationship of the emission was recorded automatically. Under these conditions the lifetime was about 1.5 min. The area under the curve, representing the total emission at 430 mμ, was measured geometrically and converted into absolute quanta units by application of the calibration factor.

The emission decay was too rapid to permit direct measurement of the spectral distribution, the unit spectral area was obtained from fluorescence data. Other experiments have shown that the fluorescence unit spectral area is at least approximately comparable with that obtained in the chemiluminescence reaction (see Figure 5).

The quantum yield was then calculated from the following equation as described in the preceding experiment.

$$Q.Y. = \frac{\left( \int_0^{\infty} I_{430} dT \right) \left( \frac{\int_{\lambda_1}^{\lambda_2} I d\lambda}{I_{430}} \right)}{[\text{molecules of oxalyl chloride}]}$$

$$Q.Y. = \frac{5.31 \times 10^{16} \times 11.5 \times 100}{0.02 \times 0.75 \times 10^{-3} \times 6.02 \times 10^{23}} = 6.8\%$$

A repetition of this experiment gave a quantum yield value of 6.0%.

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